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THE BRITISH JOURNAL OF METALS

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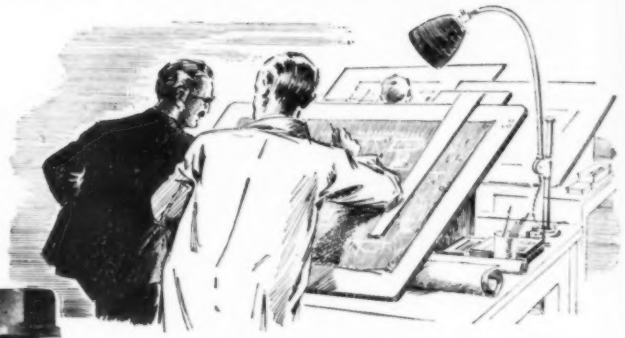

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METALLURGIA

The British Journal of Metals

(Incorporating The Metallurgical Engineer)

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METALLURGIA

THE BRITISH JOURNAL OF METALS.
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OCTOBER, 1944 VOL. XXX. No. 180

Clay as a Competitor of Bauxite

ALTHOUGH it has been known for almost a century that every ounce of the millions of tons of clay in the earth's surface contains aluminium salts from which, theoretically, the metal might be extracted, the aluminium industry has depended largely on bauxite for its aluminium source. This is not due so much to the fact that bauxite contains from 45 to 60% of aluminium oxide, compared to about 35 to 40% in high grade clay, but rather to the fact that it carries considerably less silicon and other materials that complicate extraction and increase costs.

The industry has continued to depend on bauxite despite the facts that enemy submarines operating in the Caribbean threatened to cut off all United States shipments of high-grade ore from Surinam and that supplies of low- and medium-grade in Arkansas indicated exhaustion in a very few years of wartime production, leaving still lower-grade ores in Tennessee, Alabama, Mississippi, and Georgia for even fewer years of production.

As there was a possibility that war production might have to be continued too long for the United States bauxite supply, the War Production Board was prevailed upon to authorise the erection of suitable plants for extracting alumina from materials other than bauxite. Authorisation was given for the erection of four such plants, all somewhat larger than ordinary pilot plant operations. The first of the four to get into full production was that of Kalunite, Inc., at Salt Lake City, which has been extracting alumina from alunite (potassium aluminium sulphate) since early this year for the Olin Corporations aluminium reduction plant at Tacoma, Washington. Another plant, according to *Business Week*, is expected to be in full operation at the end of this month which will extract aluminium from clay for the first time in genuinely commercial quantities. This is the new Harleyville (S.C.) plant of the Ancor Corporation.

While it remains to be seen whether the reduced need for the very high aluminium production will halt further construction of the Laramie (Wyoming) plant of the Monolith Portland Midwest Co. for the extraction of alumina from feldspar (aluminium silicate plus potassium, sodium, calcium, or boron) and of the Salem (Oregon) plant of the Columbia Metals Corporation for extracting alumina from Oregon clay, both Kalunite and Ancor have so far been given authority to proceed.

The location of the Ancor project at Harleyville was determined on plentiful supplies of limestone and white kaolin clay in the vicinity with ample power and transport facilities. Nearness to limestone deposits was as important as that of clay or power, because the Ancor process requires 2·3 tons of limestone to treat a ton of clay and only 0·45 kwh. of current to produce a pound of alumina. It takes 10 kwh. of additional electricity to produce a pound of aluminium from about 2 lb. of alumina.

Electricity is not used directly in the extraction of alumina as it is in the electrolysis of aluminium, but rather as power for rotary grinding mills, mixing mills, calcining kilns, and pumps for countercurrent filtration. The major steps in the Ancor process, which is described by its originators as a "lime-sinter method," consists of (1) preparation and mixing of raw materials, (2) furnacing, (3) leaching, (4) purification of solution (5) recovery of alumina trihydrate from solution, and (6) calcination of the hydrate to oxide, or pure white alumina powder, in a continuous operation. Coal is used as fuel.

Although the method is much more complicated than a bare outline would indicate, what it accomplishes under close laboratory control is the conversion of the 45% silica in kaolin into an insoluble compound, permitting the 40% of alumina to be leached out as a solution, and the elimination of certain salts of iron, titanium, phosphorus, calcium, magnesium and sulphur.

Ultimate costs cannot be determined until the new plant has been in full operation for several months, but is confidently hoped by the sponsors that they will be able to disprove the traditional dictum of the aluminium industry that "alumina cannot be produced from clay or other materials than bauxite at a cost that will be competitive with its manufacture from bauxite unless substantial income can be derived from by-products." They point out that the residue from their operation will be composed "mainly of dicalcium silicate with a small admixture of calcium carbonate" and that it is "no secret that this is a desirable raw material for the manufacture of portland cement." Whether the officials of the big Santee-Cooper project, which provides the power and water transport facilities, will seek to add a cement plant depends much upon the success of the Ancor operation and the possibility of its expansion in the face of resumed importation of bauxite in quantity from Surinam and the proposed mining of bauxite in Haiti.

The process adopted at this Harleyville plant gives a product suitable for processing in a Bayer plant, such as those now in use for purifying bauxite, or it can be recrystallised under pressure to get rid of the remaining silica and then treated with the recovered carbon dioxide to precipitate aluminium tri-hydrate, which is filtered off and calcined to alumina in a rotary kiln.

The fact that goods made of raw materials in short supply owing to war conditions are advertised in "Metallurgia" should not be taken as an indication that they are necessarily available for export.

Restoration of Kirov Coking Plant

The Work of Alexander Golubchick

APART from the purely military problems involved in recovering her territory from the Germans, Soviet Russia has had tremendous problems of an industrial character. Many of her great works, which had revolutionised her industrial activities, were in the hands of the enemy and, on their recapture, were in such a state of destruction that superhuman efforts were necessary to rebuild and bring them into active service in the shortest possible time.

Before the war, for instance, the Kirov metallurgical work in Makeyevka was one of the largest in the Soviet Union. Thousands of tons of coke, millions of cubic feet of gas and hundreds of tons of valuable by-products were produced daily from the coke plant. But, about nine months ago, when following the liberation of the Donbas workers, engineers and management returned to Makeyevka, the devastation they found was indescribable. They found nothing but ruins, demolished walls, broken plant and machinery, and literally mountains of debris. Before fleeing from the Donbas the Germans blew up the main factory buildings, destroyed the power station, demolished the ovens and tore up the rails on the factory premises, as well as destroying all machinery installed in the works.

The restoration of this plant was no light task, but willing hands worked day and night removing the debris and getting the building into shape. From the construction site alone some eight thousand tons of bricks and scrap iron were removed. No electric power was available, so the power developed by motor truck had to be used. In nine months, however, the engineers and workers, under the able guidance of Alexander Golubchik, director of the plant, achieved marvellous results. The fourth coke oven battery, the machinery of the main coke plant and all the machinery of the gas plant were fully restored.

This remarkable achievement was due in no small measure to the energy, skill and organising ability of Alexander Golubchik and it is noteworthy that he has received the congratulations of Marshal Stalin on the excellent work done by the entire personnel. This gifted director began his technical career in 1925, at the age of twenty-four, when he commenced the study of mining engineering at the Dniepropetrovsk Mining Institute. On qualifying, the huge construction undertaken in the first Five Year Plan period provided the young mining engineer with vast opportunities and his initiative and resourcefulness in introducing very efficient working methods into industry earned him several awards. It is particularly appropriate that the day after the Soviet Army entered Makeyevka, Alexander Golubchik, the director of the Kirov plant, should have been made responsible for its restoration.

This is only one instance of the efforts of Soviet Russia in restoring her battle scarred industries and an example of the indomitable spirit and genius of her people in achieving success.

Royal Aeronautical Society Gold Medal

The Council of the above Society have awarded Air Commodore Frank Whittle, C.B.E., Fellow of the Society, their Gold Medal for his work on Jet Propulsion. This Gold Medal is the highest award the Council can make.

Forthcoming Meetings

THE IRON AND STEEL INSTITUTE.

Oct. 24. Joint Meeting of the Lincolnshire Iron and Steel Institute and the Iron and Steel Institute at the Modern School, Cole Street, Scunthorpe (7-30 p.m.). Subject.—"Some Notes on Slags and Slag Control in Basic Open Hearth Tilting Furnaces using Phosphoric Iron," by A. Jackson.

THE INSTITUTE OF METALS.

Oct. 26. "Spectrograph Analysis," by F. G. Barker, at the James Watt Memorial Hall, Birmingham (6-15 p.m.).

MANCHESTER METALLURGICAL SOCIETY.

Nov. 15. "The Significance of Mechanical Tests on Metals," by H. O'Neill, D.Sc.

INSTITUTION OF MECHANICAL ENGINEERS.

Oct. 27. "The Influence of Engineering on Social Advancement," by Edward Reeve, M.I.M.E.

Nov. 3. "Stresses by Analysis and Adjustment" by Prof. A. J. Sulton Pippard, M.B.E., D.Sc.

Nov. 17. The Thirty-First Thomas Hawksley Lecture, "Research and Development in Aeronautics," by H. E. Wimperis, C.B., C.B.E., M.A., D.Eng.

THE ROYAL AERONAUTICAL SOCIETY.

Nov. 4. Discussion on Civil Aviation in the Lecture Hall of the Institution of Mechanical Engineers, Storey's Gate, S.W.1. The discussion, which will begin at 10-30 a.m., will be divided into sections dealing with economics, aircraft and aero engine design, route facilities, and the selection and training of personnel. The chair will be taken by Lord Brabazon.

SHEFFIELD METALLURGICAL ASSOCIATION.

Oct. 31. "Any Questions." (Sheffield Metallurgical Club at 6-30 p.m.). Members are invited to forward questions for consideration.

Nov. 7. Joint Meeting with the Institute of Welding at the Royal Victoria Station Hotel (6-30 p.m.) "Are Welding Problems—Some Notes on Metallurgical Solutions," by H. F. Tremlett, B.Sc., A.R.S.M.

Nov. 18. "Technical and Economic Problems in the Heavy Iron and Steel Industry," by R. A. Hacking, M.Sc.

INSTITUTE OF BRITISH FOUNDRYMEN.
LANCASHIRE BRANCH.

Nov. 11. "Gravity Diecasting," by A. R. Palmer.

ERRATUM

Dr. A. C. Vivian, the author of the article "The Relationship of 'Rheology' to 'Strength of Materials'" in the issue of September last, wishes to apologise for his oversight in the use of the word "strain" instead of "stress" in the seventh line of the third paragraph on page 239 of our September issue. Lines of equal *stress* on the surface in question will be parallel to the strain-time plane, and the slope of such lines at any point along their length is the ratio of the increment of strain to the increment of time. This, as Poisson and Maxwell pointed out, is the same as the velocity gradient; and the ratio between the stress and the corresponding velocity gradient is nothing but the viscosity.

Essential Characteristics of Controlled Atmospheres

By W. D. Vint

The demands for greater multiplicity of light steel articles is growing and, in view of the necessity for cold-working operations in shaping them, and the rigid physical specifications demanded, bright annealing as an intermediate stage in production has become a major phase in manufacturing technique. Bright annealing can be carried out in any type of non-oxidising atmosphere, and the author discusses the essential characteristics of these atmospheres.

BRIGHT annealing as an intermediate stage in the production of light steel articles has only comparatively recently attained an important position in the realm of heat treatment procedure. The demand for greater multiplicity and greater numbers of light steel articles is growing almost daily, and, in view of the necessity for cold-working operations in the shaping of these articles and the ultimate physical specifications demanded on the finished article, inter-annealing has become a major phase in manufacturing technique.

Briefly, the process of bright annealing can be defined as ordinary annealing carried out in any type of non-oxidising atmosphere such that the ensuing product is free from scale or discolouration and retains its original surface condition. The complete exclusion of all traces of free oxygen is a primary condition and there is little doubt that in the modern type of controlled atmosphere plant in which hot reduction comprises the main principle, oxygen is burnt out to a final negligible quantity, thereby satisfying the need for complete non-oxidisation.

Many bright annealing plants possess the disadvantage of long atmosphere gas supply lines and at the points of application to the furnace itself several points of air ingress may be present. Also, low initial flow rate and pressure drop result in a very low positive pressure at the furnace. In the majority of annealing furnaces some provision is also made for circulating the atmosphere inside by means of a fan, necessarily powered by a revolving shaft from outside. Here again difficulty is experienced in preventing air ingress at the point of entrance of the shaft. A theory advanced, implies that the partial vacuum caused by upward rush of atmosphere gas from the fan blades enables air to enter at any tiny leak in the base or shaft packing.

Some types of annealing furnaces cannot utilise the efficient water or oil seals and therefore resort to sand seals with a resultant increase in the possibility of air ingress. These particular difficulties can hardly be overcome except by a drastic redesign of plant or by the much more simple expedient of employing an atmosphere gas of greater positive presure. To counterbalance any air ingress tendencies a relatively high pressure atmosphere gas of at least 5 ins. W.G. is generally needed ; this is not to imply, however, that the regenerative type of atmosphere plant in which return gas pressures may be as low as 0·05 ins. W.G. is not suitable for bright annealing, rather should the possible limitations of that particular type of plant be appreciated

Types of Atmosphere Plant

Perhaps a brief description of the principles involved by three types of atmosphere plants with special reference to their singular gas characteristics will serve to elucidate several of the problems liable to be encountered.

Firstly, the cracked ammonia regenerative system—ammonia gas is led into an electrically heated, thermostatically controlled dissociater or cracker and split by catalysis into its component parts of hydrogen and nitrogen. The resultant gas comprising 75% hydrogen and 25% nitrogen is then passed into a burner chamber and burnt with a limited air supply such that the hydrogen figure is reduced to a more convenient value of say 6–10% Water formed by the reaction is condensed and removed from the system by passing the gas through a cooler. Moisture is then almost completely removed from the saturated gas by passing through water cooled silica gel driers. At this point the gas is ready for distribution on the plant and a return system via oil separators and cleaners ensures its almost complete recovery. Oxygen picked up by the purging of pots or furnaces is eliminated by virtue of the reducing conditions maintained inside the burner.

Secondly the burnt town's gas type of atmosphere plant merits a brief description. Ordinary town or coke oven gas is passed into a refractory lined chamber, burnt with a limited air supply and the resultant products of combustion controlled by an air/gas proportioning value are cooled, dried, desulphurised and supplied to the annealing furnaces. No return system by which gas after use can be returned to the plant is here possible, therefore the gas is burnt at the purge outlet.

Thirdly, a more uncommon type of plant is the blast furnace gas cracker. In cases where blast furnace gas is easily accessible and cheap, the construction of a B.F. Cracker is worthy of consideration and is possessive of several marked advantages over the other two types of plant. Blast furnace gas generally contains a small percentage of oxygen, figures between nil and 0·20% are fairly average. Even this small percentage of oxygen can quite effectively "blue" the surface of steel and the task of removing this oxygen is accomplished by passing the gas through heated tubes (at about 800/900° C.) containing steel swarf. Either one or both of two reactions occur to effect the combination of free oxygen with carbon monoxide to form carbon dioxide. The oxygen can form iron oxide on the steel surface which is instantly reduced by the carbon monoxide, or the carbon monoxide can combine directly with the oxygen.

B.F. gas flow rate is so adjusted that there is no overloading and no possibility of oxygen passing through uncombined. As before, the gas is cooled and dried by passing through water cooled silica gel driers then supplied to the annealing surfaces. Owing to its cheapness no return system is necessary, therefore, after use the gas is burnt at the purge outlet.

Essential Characteristics

The essential characteristics of bright annealing atmospheres are many and it will be well to enumerate the most important first :—

Absence of Free Oxygen.—Something already has been said upon this prone necessity. In the three types of plant briefly described, providing no leaks or points of air ingress are present and strong reducing conditions are maintained in the burners no trouble with oxygen should be encountered. Owing to the large proportion of air delivered to the burner the partially burnt town's gas plant is the most likely to give trouble. The following ingoing and outgoing gas analyses show the extent to which town's gas can be burnt to provide a satisfactory bright annealing atmosphere.

A high CH_4 content in the burnt gas is liable to produce sooty deposits on the surfaces of annealed material, therefore this figure is maintained as low as possible. Care should be taken to ensure that increasing air proportion to fulfil the above condition does not lead to over-correction and hence give rise to resultant oxygen in the burnt gas. A point well worthy of mention here is method of testing the gas for oxygen. The ordinary type of Orsat gas analysis apparatus is not sufficiently accurate for the purpose as correct values between nil and 0·10% cannot be obtained. The Haldane Air Analysis Apparatus is much more suitable and accurate figures as low as 0·01% are easily obtainable. Oxygen percentages should never be allowed to exceed 0·01% ; 0·02% of oxygen will certainly discolour steel surfaces under certain conditions.

TOWN'S GAS ANALYSIS.		EXIT BURNT GAS ANALYSIS	
CO_2	3·6%	CO_2	7·4%
O_2	Nil	O_2	Nil
CnHm	2·1%	CnHm	Nil
CO	13·5%	CO	7·9%
CH_4	17·1%	CH_4	0·6%
H_2	51·6%	H_2	6·0%
N_2	12·1%	N_2	78·1%
	100·0%		100·0%

Moisture :—The moisture content of a protective atmosphere can, in some cases be quite important. For instance in the annealing of high-carbon steels an excessive moisture figure is quite often instrumental in causing a high degree of decarburisation on the steel surfaces. Decarburisation itself is not produced solely by the presence of moisture, other factors contribute and accentuate the reaction but with the allied help of moisture a highly decarburising condition can be set up. Some annealing plants, where the presence of moisture in the atmosphere gas does not affect the annealed article dispense with the silica gel drying section of their plant and pass the undried gas straight to the furnace. In many instances, however, where moisture does affect finished material great care is taken to ensure that the gas is as dry as possible.

The general gas drying arrangement consists of a pair of silica gel driers (preferably water jacketed) each drier being used in circuit alternatively, whilst the other is regenerated (i.e. moisture removed) by electrically heating for a specified time. The length of time in service before regeneration becomes necessary is best discovered by experiment ; generally the time can be reckoned at between 12 and 18 hours. The significance of providing driers with water jackets is well illustrated by the following average figures for jacketed and unjacketed driers :—

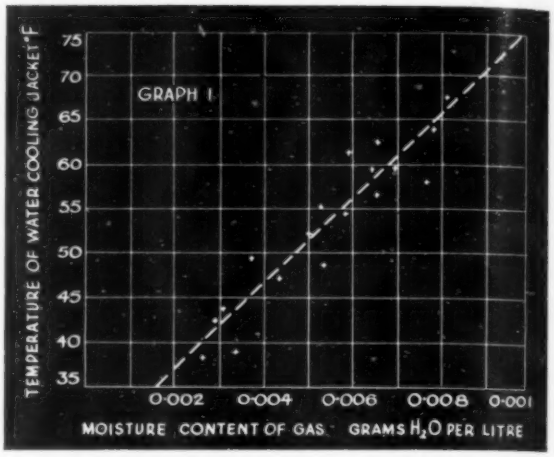
AIR COOLED Average Moisture Content of Gas during 12 hours. Gms. H_2O/litre.	WATER COOLED. Average Moisture Content of Gas during 12 hours. Gms. H_2O/litre.
0·00432	0·00129
0·00560	0·00190
0·00486	0·00113
0·00439	0·00144
0·00510	0·00126
0·00363	0·00088

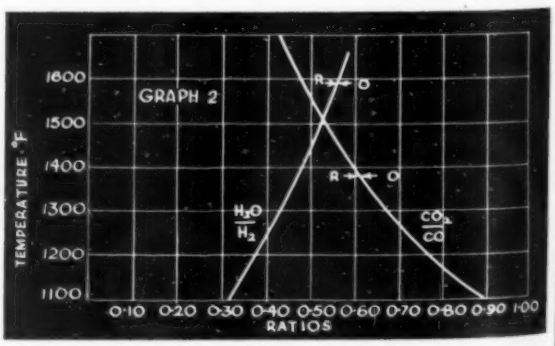
A certain amount of variability is to be expected between figures of each set of results as surrounding air or water temperatures vary from day to day.

The efficiency of silica gel as a drying medium depends to a very great extent upon its surrounding temperature. Graph No. 1 illustrates this point and the extremes of water jacket temperatures typify average summer and winter conditions. In all cases, moisture estimations were carried out on a drier which had been in operation for 18 hours.

To ensure satisfactory low moisture figures the surrounding jacket must be kept as cool as possible. Generally speaking, the maximum figure of 2·5% H_2O by volume should be made the limit ; below this, little serious decarburization directly due to moisture should be experienced. Gas containing a high degree of moisture is under certain conditions oxidising and the steel surface reaction is as follows :—

$$Fe + H_2O \rightleftharpoons FeO + H_2$$





This reaction is reversible. If H_2O is in excess the reaction will progress towards the right with the formation of H_2. If H_2 is in excess the reaction will progress to the left with the formation of H_2O. In either case, reaction will proceed until a point of equilibrium is reached. The equilibrium constant (i.e. H_2O/H_2 ratio) varies in magnitude with temperature and Graph No. 2 plots these two factors. In any protective atmosphere a ratio H_2O/H_2 will indicate at once whether or not the combined effects of H_2O and H_2 is oxidising or reducing.

Hydrogen :—In the case of ammonia derivatives, and partially burnt town's gas, hydrogen is the main reducing factor. The actual percentage of hydrogen is easily varied in both types of plant but should be governed by two factors :—

(a) In conjunction with percentage moisture H_2O/H_2 ratio should be situated on the reducing side of the curve. With a high H_2 figure moisture can be allowed to creep up accordingly. With a low H_2 moisture must also be low. (See Graph No. 2.)

(b) Up to about 15% in the case of ammonia derivatives or atmosphere containing no other combustible gas, hydrogen is fairly non-explosive. Above this figure there is certainly some likelihood of explosion, and the danger is intensified by the introduction of methane or other hydrocarbons to the gas.

Cracked blast furnace gas rarely contains more than 3·5%H_2 and the usual value is about 2·3/2·8%, therefore the main reducing property is not due to hydrogen.

Carbon Dioxide and Carbon Monoxide :—With gases containing the above constituents a suitable ratio must be arranged such that a reducing action is set up. The reaction between the gas and steel is reversible and as follows :—

$$Fe + CO_2 \rightleftharpoons FeO + CO.$$

With reference to Graph 2 it will be observed that, as before, the reaction progresses in the opposite direction to the predominating constituent. Ammonia derivatives operating on the return or regenerative system usually contain small percentages of CO_2 and CO picked up by the partial combustion of rolling oils and lubricating soaps, etc., present on the surface of the steel. The analysis below represents a typical gas composition, the sample being procured from a point on the outgoing line in a closed ammonia gas return system.

The CO_2 and CO percentages are not usually high enough to cause much difference in oxidising or reducing properties. The CO_2/CO ratio, however, is very important in the case of partially burnt town's gas and cracked blast furnace gas.

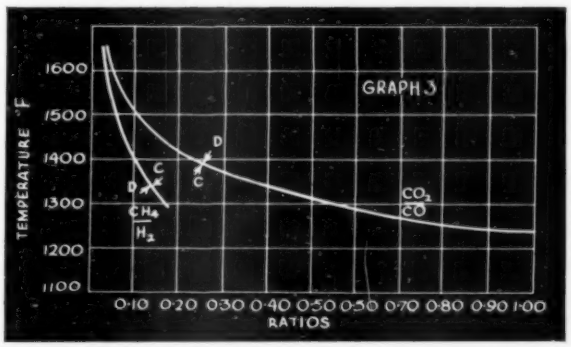
ANALYSIS.	
CO_2	0·21%
O_2	Nil
CO	0·18%
CH_4	0·24%
H_2	6·34%
N_2	93·03%
	100·00%

A typical cracked B.F. gas contains CO_2 10·2%, O_2 nil, CO 29·8%, H_2 2·5%, N_2 57·5%. Carbon monoxide is the chief reducing factor and is counteracted or offset by the percentage of CO_2. The composition of B.F. gas cannot be changed easily, and the CO_2/CO ratio must therefore remain a fixed unalterable quantity. With partially burnt town's gas CO_2 and CO percentages can readily be adjusted by controlling air : gas ratio at the burner ; increasing air input causes a greater degree of combustion with a resultant rise in CO_2 and drop in CO, i.e. the CO_2/CO ratio tends to fall on the oxidising side of the curve ; by decreasing air input less town's gas is burnt, CO_2 falls and CO rises, therefore the ratio will tend to fall more towards the reducing side of the curve.

In addition to their reducing and oxidising properties CO_2 and CO can produce decarburising and carburising reactions respectively :—

$$C + CO_2 \rightleftharpoons 2CO$$

If the CO_2 of the CO_2/CO ratio is high, reaction will proceed to the right with the resultant loss of carbon to the steel, and conversely if the CO of the ratio CO_2/CO is high reaction will proceed to the left with a gain of carbon to the steel. For investigating the carburising or decarburizing properties of an atmosphere gas with regard to CO_2 and CO, Graph No. 3 should be consulted.



Methane :—Cracked B.F. gas is practically free of hydrocarbons and can be neglected in a consideration of the effects produced by methane. Burnt town's gas contains some methane from the partial combustion it undergoes and closed system ammonia plants pick up a certain quantity during the cracking of rolling oils or lubricating soaps. The methane content is important in that it is responsible for carburisation and carbonisation. It s effect is opposite to the decarburising effect of hydrogen and the reversible reaction is as follows :—

$$CH_4 + 3\,Fe \rightleftharpoons Fe_3C + 2\,H_2$$

The CH_4/H_2 ratio should therefore be calculated if an accurate assessment on the decarburising or carburising properties of the gas is to be considered. Graph No. 3 supplies the necessary information on the equilibrium constants with their relationships to temperature.

The carburising properties of high methane percentages can be counteracted by increasing hydrogen percentages, until the equilibrium constant is reached. In actual practice using partially burnt town's gas as an atmosphere, methane contents above 0·8% were found to give trouble by depositing soot on the surface of the material.

Sulphur Compounds :—An additional complication usually encountered when dealing with the products of partially burnt town's gas is the necessity for removing sulphur compounds from the gas before delivery to the plant. Town's gas contains varying amounts of sulphur as CS_2, H_2S, SO_2 and other organic sulphur compounds. On partial burning some of the sulphur is oxidised to SO_2 and the remainder, mostly H_2S, is removed by passing the gas through vessels containing bog iron ore, (activated charcoal is a better reagent if it is desired

to remove all the sulphur). Generally speaking, sulphur as H_2S has little effect upon plain carbon steels until a figure of 0·003% is reached and it is at this point that a greyish matte surface of iron sulphide is produced on the surface of the steel.

Owing to the suddenness in which the efficiency of iron bog ore can fall it is wise to make periodical tests for H_2S on the burnt town's gas before and after desulphurising. Fluctuations in town's gas quality can give rise to erratic sulphur figures in the burnt gas. For instance, should the calorific value of the town's gas alter, no automatic adjustment of the air supply ensures a continuance of the same degree of combustion therefore a higher percentage of unoxidised sulphur compounds pass into the bog iron ore vessels. This results in overloading, and subsequently a higher H_2S content in the outlet gas.

Effect of Rolling Oils and Lubricants

Frequently, bright annealing forms an intermediate stage in the drawing and rolling of steel products and it is this fact that causes a great deal of material to be transferred to furnaces with varying amounts of rolling or lubricating compounds upon its surface. Obviously then the formation of hydrocarbons caused by the cracking of these soaps and oils must modify the otherwise straight chemical reaction between the gas and steel. The extent to which the adulteration of cracked ammonia gas by the products of the cracking of oil vapours and soap lubricants occurs, may be discerned by a study of the return gas analysis shown below. Uncontaminated cracked ammonia gas should contain no CO_2, O_2, CO, or CH_4 but the pick-up of these gases and the loss of some H_2 (original H_2 figure is usually between 6 and 7%) is considerable. Oxygen certainly is destroyed at the burner by the reducing conditions maintained therein, but CO, CH_4, and CO_2 can partly react to form complex organic compounds. Most of the CH_4 and CO should be burnt as they mix with the regulated air supply in the burner chamber with a resultant increase in CO_2 percentage :—

RETURN GAS ANALYSIS

	1	2	3	4
CO_2 ..	1·62%	1·83%	1·85%	1·77%
O_2 ..	0·39%	1·30%	0·83%	0·73%
CO ..	0·34%	0·66%	0·59%	0·34%
CH_4 ..	1·97%	2·80%	2·13%	2·01%
H_2 ..	5·20%	4·30%	4·14%	5·33%
N_2 ..	90·48%	89·11%	90·46%	89·82%
	100·00%	100·00%	100·00%	100·00%

The "build-up" of undesirable contaminating gases should be minimised by purging annealing furnaces during the heating-up period at a temperature when oils and lubricating soaps begin to decompose. By adopting this procedure a partial elimination of CO_2, CO and CH_4 should be obtained.

Economical Uses for Discarded Broken Tungsten-Carbide Tool Tips

By W. M. Halliday

These notes describe a number of useful ways in which broken fragments of fractured carbide tool-tips may be utili ed with great advantage. By careful selection it is possible to employ such broken tips in connection with a number of ordinary workshop tools, thereby gaining the benefits of the high abrasive resistance of this material, as well as economically conserving its use.

IN most machine shops and engineering works where cemented carbide is used as a cutting material for machining operations, there tends to accumulate a stock of broken pieces which are taken from damaged and fractured tools from time to time, and which are sometimes held to be almost useless.

It is certainly not generally appreciated that numerous other ways of utilising the outstanding ability of this material to resist wear, other than as a direct cutting medium are open to the enterprising and ingenious tool-room supervisor.

Apart from the definite and substantial advantages to be gained by adopting such measures in the shape of improved tools and equipment, as will be explained later, such a practice will be found especially convenient and time-saving in these days of supply difficulties, and delivery delays, and increased cost of materials. Judiciously applied such a policy may afford very considerable financial savings in addition.

Sorting and Selecting Broken Tips

At the outset it will be of assistance to describe the methods employed in one tool-room of the author's acquaintance in dealing initially with all fractured and broken pieces of carbide tool tips which are received at the tool stores from time to time.

All such bits are removed as soon as possible from the returned tools ; partly to obviate further damage to the tip likely to result from accidentally knocking against other metallic objects if left lying about on benches for a time ; and also for the reason to prevent the loss of loose pieces of a broken tip which might prove very useful for another purpose.

These pieces are then placed in a suitable small receptacle, and once per week the tool-room foreman makes a careful examination of the small stock with a view to selecting those pieces likely to be of any value.

His aim throughout such examination will be threefold. First he will endeavour to choose all those portions

of cutting tips which are large enough to permit of further use as tips for lathe cutting tools. Secondly, he will attempt to select those smaller and less uniform sizes and shapes of broken bits which will be applicable to other purposes, some of which will be described later. Thirdly, he will examine all pieces for cracks, or apparent flaws which are of sufficient magnitude as to render the piece entirely unsuitable for any other purpose.

Respecting the first object mentioned, it should be constantly borne in mind by those responsible for the use and application of carbide tipped tools, that very often a damaged *heavy-duty* tip may provide thinner pieces which may often be employed with success and economy upon *light-duty* operations. Thus a large cross-sectioned *roughing* tool tip may often break in such a manner as to enable a very useful smaller cross-sectional piece for *finishing* operations.

This point should constantly be watched, particularly now that grinding this material by means of diamond impregnated wheels has advanced sufficiently to make the forming of cemented-carbides both a practical and economical tool-room operation.

In searching for cracks and flaws it is emphasised that it will be advisable to use a strong magnifying glass because in numerous instances the nature of the fracture suffered by tool-tips gives rise to a number of very minute hair-like cracks, they appear as faint lines even under the glass, and which are not visible to the unaided eye. Usually though, these cracks tend to open or extend if the piece is subjected to excessively abnormal temperature variations or pressures.

The sorted pieces are then stored ready for future use in suitable separate containers which practice will save time by facilitating the choice of a tipping piece at a later date.

Those considered useless are of course not discarded immediately, but held in stock for a few months until the quantity becomes excessive. It will be advisable, however, to retain possession of a few of the largest pieces even though it is known that cracks are present, because on some articles such cracks may not prove deleterious, and in addition it should be borne in mind that ordinary brazing will seal off all cracks quite effectively for many purposes other than metal cutting.

Scribing Tools.—The first alternative use which the present writer has adopted fairly extensively relates to the tipping of the ordinary scribing tools employed by the engineer. These tools include both the scribing gauge block of well-known pattern and function, as well as straight hand-scribers used for marking off purposes.

For this operation broken pieces of carbide material having a length of anywhere from $\frac{3}{16}$ in. to $\frac{7}{16}$ in. were chosen. As the diameter of such scribing tools is usually about $\frac{1}{8}$ in. any piece between the above lengths having a cross sectional area equivalent there-abouts to the cast steel rod used for scriber will suffice.

The methods of attaching such tips will be of interest. Before brazing the tips into position the ends of rod should first be prepared in the following manner. Each end of rod to receive a tip is filed dead square and back to full diameter, then a small saw cut not more than $\frac{1}{16}$ in. wide is run centrally across the end of rod, and extending for a depth of about $\frac{3}{16}$ in.

One end of the tip for that end is then thinned down until it can be lightly tamped into the saw cut for at least two thirds the depth of the latter.

The purpose of this saw-cut is three-fold. First it ensures that the small piece of material may be snugly held in correct position throughout heating necessary for brazing. Then it ensures additional anchorage for the tip, and finally the brazing metal can effectively surround the entire tip to provide a stronger bind, which will be necessary in the case of such small diametered rod being tipped.

The rod and socketed tip is then carefully heated up (preferably in a small hot Bunsen jet directed some distance back from the tip) and both liberally coated with brazing metal. Afterwards the tool is allowed to cool without quenching, and when cold is ground up to remove the excess brazing material as well as to form a point on the exposed carbide tip.

In this manner it is possible to obtain a very strong joint of the two parts enabling the tip to give service for a long period without flinching. The point should rarely need regrinding unless dropped from a good height, or similarly ill-treated.

Vernier Height-Gauge Knife Scribers.—Again in respect to the knife-shaped scribers commonly used in conjunction with the vernier height gauge, troubles often arise due to the wear of the sharp marking edge of the cast-steel knife.

This may lead to costly errors because if the knife is worn badly the scribed line ultimately made will not be at the precise height distance given by the vernier setting, whilst in addition, a blunt knife edge will cause a thick line to be made which will also render accurate laying-out difficult.

In order to overcome such disabilities the writer employed the same procedure of tipping with broken pieces of carbide material.

For this purpose very thin portions were selected, this dimension rarely exceeding $\frac{3}{32}$ in. As near as possible rectangular outlines were also chosen in order to reduce the need for grinding the tip.

The knife itself was ground carefully to provide a seating for the tip, by making a step clean across the requisite edge and of course approximately the same depth as the thickness of the tip.

Careful attention was given to this question of seating, the tip being so ground until it could sit down flat and with one edge abutting smartly against the square side of step.

It was then brazed into position, and after cooling, was ground up to original shape of the knife, the cutting edge being afterwards lapped.

By this means many of the troubles already mentioned were entirely eliminated and a much longer service was obtained from the knife before the need arose for resharpening, which, when it did occur, merely consisted of a second lapping process to restore the cutting edge.

Flat Metal Scrapers.—Numerous widths of flat hand scrapers are usually employed by the tool and die maker, whether engaged upon press-tool, die-casting, or plastic dies, and here again in connection with these useful and important tools the writer was able to introduce a large number of discarded carbide tips with great advantage.

Such scraping tools range in width from $\frac{1}{4}$ in. up to 1 in., and it was found a very simple matter to secure suitable tips from broken tool tips which proved quite satisfactory for the purpose.

Very thin tips were chosen, usually not more than $\frac{3}{32}$ ins. thick, and of course as near rectangular in outside shape as possible.

Again the shank of the scraper was thinned down at one end to form a stepped seat wherein the tip could reside, it then being brazed in normal manner into this position. After the shank and its tip have cooled down to room temperature the tip portion may be ground up to required cutting edge shape afterwards being lapped on both sides and extreme end surfaces.

Extremely handy, durable and smooth cutting tools were thus obtained which were found to be a great improvement over the ordinary cast-steel or high-speed steel types formerly used.

Pin and Gap Gauges.—The smallest pieces of broken carbide tips will come in extremely useful for the tipping of all kinds of gauges, notably the straight pin, and bent-over gap or spigot gauges. Large numbers of these latter have been tipped with very successful results by the writer, and have been found to give twelve months or more continuous daily service without any visible signs of wear.

Contrasting this with the checking and correction service previously required when ordinary hardened tool-steel gauges were used, it will be appreciated the valuable savings which can be effected by this simple means, which savings are still further augmented when it is recalled that supposedly valueless material was employed for the tips.

In regard to both pin and gap gauges the method of tipping was very simple and expeditious. The smallest pieces were used for the pin gauges, which latter were generally of rectangular or square cross-sectioned tool steel with the ends thinned down to about $\frac{1}{8}$ in. diameter, thus it will be appreciated that the tip is similarly of small dimensions.

First the pin gauge was softened at each end in order to remove about $\frac{1}{8}$ in. from each end. This amount of tip length was found to be necessary to avoid gauging troubles occurring in the unusual event of a tip being ripped out of place and passing unnoticed by the inspector.

Centrally across each end a shallow vee-shaped recess was then filed, being approximately half the width of rod end at its widest part. The tip was then carefully ground until one end formed a matching vee shank. The tips were then brazed in, by resting the gauge body on a flat plate, with a suitable heavy object at each end, one bearing on to the loose tip, the other against opposite end of gauge, in this manner serving to hold the tip in correct position in vee. An ample supply of brazing metal was given, surrounding the entire tip as much as possible and building up especially over the vee recess.

After cooling, the tipped end was ground to circular or other desired shape sufficiently to uncover about $\frac{1}{8}$ in. of the carbide tip. Final sizing of the completely tipped gauge to secure proper length being performed on a diamond wheel.

The vee recess was formed across the end of the gauge body so as to lie at right angles to the normal direction of applying the gauge to workpiece. This ensures that least pressure is imposed on tip tending to push it out in an endwise direction.

In the case of bent-over gap gauges a somewhat similar procedure was employed, with the exception that a rectangular seating was ground on the contact end of gauge into which a thin flat rectangular piece of material was seated.

Larger pieces of course are applicable in the case of this type of gauge. The tip should be bedded well back against the vertical side of seat, as well as being bedded down until resting firmly and flatly on bottom of the seat. Copious brazing material is also applied and, if desired, could be used as a build-up if considered necessary to offset any weakening suffered by making the seat for the tip.

Great savings in respect of time needed for checking and correcting these tools, as well as improved accuracy, and much greater reliability were the outcome of this simple inexpensive adaptation of previously considered worthless broken pieces of cutting material.

Using Carbide Tips on Jigs and Fixtures

The jig designer and tool engineer will also find innumerable opportunities of using such broken pieces of carbide tips in connection with fixtures and jigs, etc., in order to avoid wear and associated errors on all essential locating, or positioning points on such appliances. Thus, on jigs having ledges or sides formed to serve as abutments for a machined surface on the component so that it shall be accurately positioned for some ensuing machining operation, it will often be found very advantageous to introduce a number of pieces of carbide material at specified points, brazing these into place so that they form the wear-resisting abutments for the article.

Again, in the case of milling fixtures having to take recessed components over a circular raised spigot, it will be found very useful practice indeed to provide a number of carbide material inserts at equi-distant spacings around the spigot. The turned spigot should be left about $\frac{1}{8}$ or $\frac{1}{2}$nd larger in diameter than the finished size, then four, six or even eight small rectangular seats are milled, evenly spaced around its circumference, into which are tamped lightly small pieces of carbide material, these finally being brazed therein. To finish off the fixture the spigot will have to be ground to final size, and in this way there will be provided a number of points about the spigot highly resistant to wear and abrasion. The writer has used this method on many occasions to eliminate errors and difficulties arising from wear, which formerly often reached costly proportions with cast-iron, or ordinary hardened steel jigs and fixtures.

By giving a little thought and consideration to many jig problems of wear it will be possible to introduce the use of cemented carbide materials with great advantage, and, if space permitted, several interesting applications could be given from the writer's own practical experience.

Tipping Floating Sizing Cutters

On the split type floating cutter or sizing reamer so widely employed for producing smooth surfaced and accurately sized holes, it is advisable to have carbide tips, as indeed all modern manufacturers now supply. Nevertheless there must be large numbers of hardened high-speed-steel cutters still in use, and the writer has often tipped such tools with great satisfaction and improved service. Here again carefully selected fractured fragments will be found applicable in many instances, especially in connection with small size cutters.

If high-speed-steel cutters are to be tipped it may sometimes be necessary to soften the bodies so that a suitable seating may be machined on each portion of the tool.

The selected tip should next be ground flat on its underside so as to bed down flat into seat. It should then be brazed into position and finally ground and lapped or diamond wheel ground to final shape.

In brazing some care will have to be exercised to avoid overheating the body of tool, and as far as possible the heat should be concentrated to as small an area as practicable surrounding the actual tip. If the whole body of tool is made generally hot there will certainly be some size variation when tool has cooled. Usually high-speed steel shrinks a small amount, but even though this may only be two or three "thous" it will be sufficient to cause dangerous slackness in the slot in bar when tool is finally assembled, with the result that uniform diametered holes cannot be reamered due to the side wobble of tool.

Cutters of the solid type can similarly be tipped using the same procedure. The same applies to boring tools for use in the lathe. Often it will be advantageous to make up a tool out of a single length of material, making each end to cut and using this for securing a sized hole at one pass. By tipping such a tool at each end it will be found to withstand wear and to maintain its original size much longer, as well as permitting faster cutting speeds and feeds to be used.

Conclusion

Whilst the foregoing notes by no means exhausts the variety and types of application of fragments of carbide tips, space precludes further descriptions. One or two final notes are however desirable, in order to indicate ways whereby inproved conservation and better usage of such tipped tools can be secured.

The first point refers to grinding of tipped parts. As is now widely known cemented carbide material heats up very quickly while being ground, and frequently immersion in cold water is resorted to as a method of cooling the tool and shank portions. Such malpractice will inevitably ruin a tool equipped with a new carbide tip even though it be of the most robust capacity.

In the case of broken pieces of tool tip used again in similar manner to those already described, such a drastic method of cooling will be doubly serious because, as previously intimated, a fractured tip may possess innumerable minute cracks invisible to the naked eye but which may be worsened to such effect by quenching the tip in cold water as to cause it to break up altogether. Especial care is therefore necessary when grinding up such tipped tools. After brazing they should not be quenched but permitted to cool gradually ; and preferably should be ground wet, with an ample flow over the tip portion, throughout all grinding, so that the tip is not permitted to undergo undue temperature rise. If the diamond wheel is employed it should never be run dry because this type of wheel is fairly fast cutting on carbide tip material and without ample water, or other coolant, heat will be quickly generated.

The final word concerns a simple method of indicating that tools have been tipped with cemented carbide material in order that greater care will be taken in handling and using them. This is accomplished by means of a band of paint of a prominent colour, red in those instances mentioned. The paint should be applied at a point fairly near the tip itself, and arranged so that it did not cause interference in any way with the use or function of the tool or gauge.

It is hoped that enough has been written to serve as an indication to others interested in the numberless ways in which hitherto unused but valuable pieces of carbide cutting tip materials may be employed to produce improved accuracy, longer life, resistance to wear or abrasive action, reduced stoppages for resharpening, or correction of a tool, and so on, as well as making valuable auxiliary use of an expensive material now in short supply.

Magnesium from Asbestos

ACCORDING to current statements in the American and Canadian press, the new Wildman process for producing magnesium chloride from asbestos is now actually operating in Canada for the production of magnesium metal.

It is rather a curious thing that asbestos, therefore, which is used extensively in the manufacture of fire-fighting equipment is also being used for making a metal used in the production of incendiaries.

In the production of asbestos for use in asbestos-cement goods and asbestos textiles and the like, a large amount of unusable material is produced and in Canada, the world's principal producer, as well as in other countries, nothing could formerly be done with this surplus, except to dump it.

It has been calculated that about 20,000 tons of asbestos waste must go to the dumps every day in Canada, and that there is accumulated a dump ofmore than 200,000,000 tons of it. The magnesium content of this waste is not stated, but chrysotile asbestos has a theoretical content of about 24% and even allowing for the fact that we are dealing with an ore and not the pure mineral, it is manifest that the magnesium content of this dump is very substantial and of course has the great advantage of availability, and the fact that the rock is already crushed up to a certain degree, important factors compared with the cost of preparing source materials such as brines and seawater.

A Montreal chemist, H. G. Wildman, is stated to have originated the idea of recovering magnesium chloride from these asbestos tailings, and the laboratories of the Dominion Bureau of Mines as well as officials of Shawiningian Chemical Ltd. have also been taking a hand in the investigations.

The Bureau's experiments and pilot-plant investigation have confirmed the feasibility of the process which consists in principle of crushing and concentrating the magnesium silicate mineral and then leaching it with hydrochloric acid to yield magnesium chloride solution, which in turn is amenable to the recovery of the metal by evaporation and electrolysis. By-products resulting from the process are said to include salt cake, chlorine, chrome-nickel, iron oxide and fine silicon.

The plant necessary for producing the magnesium chloride is stated to be relatively simple and that if all the 20,000 tons a day of waste were treated, it would yield about 3,000 tons of magnesium metal per day at a cost of about 15 cents per pound.

Spectrographic Work in an Engineering Laboratory

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Rapid and accurate methods of analysis are necessary in all branches of metallurgical industry. In recent years a large number of less common elements have been introduced in alloys and generally they add to the complexity of the analyst's task. In many cases the chemical method is long and laborious, for such cases the spectrographic method is recommended and the experience of the author in applying this method to solve the difficult day to day problems in an engineering works is of special value in obtaining reliable results in the minimum of time.

Introduction

MOST of the articles already published on spectrographic analysis apply to what might be termed the economic use of the method. Where very large numbers of, say, steel analyses have to be supplied, the spectrograph offers a time and labour-saving alternative to ordinary chemical analysis for the metallic constituents. The same applies to the mass analysis of aluminium alloys. Similarly, anyone faced with the analysis of large numbers of alloys consisting of a major element, say, lead with small amounts of several minor elements, such as antimony, tin, etc., would probably find it profitable to develop the use of the spectrograph. In the author's laboratory such conditions do not exist. Samples come in twos and threes of any one alloy in a day and in most cases these numbers would not in themselves justify departure from ordinary laboratory procedure.

The purpose of this article is to describe some of the rather miscellaneous applications of the spectrograph by which it has supplemented rather than replaced older methods of examination. The instrument is used as a general purpose tool which readily and quickly affords information difficult to arrive at by other means.

Equipment

The equipment used is a large Hilger Littrow spectrograph, with Judd-Lewis comparator for identification of lines and for visual comparison of line intensities. A Hilger non-recording micro-photometer is available for the measurement of line intensities in quantitative work.

The smaller size of spectrograph would do much of the work on brasses and aluminium alloys, but where materials high in iron or nickel have to be included, the greater dispersion of the large-size instrument is necessary.

All the work referred to in these notes is done in the ultra-violent region, hence it is always necessay to expose and develop a plate.

Scope of Work

It might be explained that the work of the Cathcart laboratory is concerned not only with the manufacturing operations in the factory but with the service behaviour of the products. All abnormal occurrences of any kind whatever, corrosion, wear or breakage reported by customers are referred to the laboratory for report. As a result the department is called on to examine materials arising from pumps, evaporators, heaters, air compressors, etc., engaged in power production on land and sea and also in a wide range of industries from food production to gas manufacture. From all these fields as well as the foundries, smithy, welding, plating and heat-treatment departments in the works, a very mixed collection of samples reaches the laboratory in the course of a year.

An attempt will be made to classify this spectrographic work though the sub-divisions are neither precise nor complete.

Qualitative

(*a*). *Where nature of material is not known.* Even when a quantitative analysis must be obtained finally, it is often necessary to do some qualitative testing before proceeding very far. This preliminary work may be quite lengthy.

A good example of this is the coating on electrodes for arc welding. These coatings vary widely from maker to maker. Some contain over 50% TiO_2, others have none. With samples of this nature, preliminary spectrographic survey is well worth while. Another example is refractory materials, which may contain ZrO, TiO_2, Cr_2O_3 in addition to the usual SiO_2, Al_2O_3, etc. All refractories require a fusion before even a rough qualitative examination can be made. With the spectrograph it is possible to say which elements are present in quantity and which are mere traces. This information allows the analyst to plan his methods with the assurance that he is neither missing some constituent which is in the sample, nor doing needless work looking for ones which are absent.

(*b*). *Identification of materials.* Even in the best regulated works, doubt does arise occasionally whether material is as labelled. Labels and paint marks can disappear, errors can creep into store cards, and for many reasons samples are frequently received for indentification or verification.

The steeloscope, a small spectroscope for the rough classification of certain alloy steels by means of lines in the visible band, has proved to be a valuable tool for the range it covers. The same type of thing and much more can be done with the larger instrument but not so quickly since a plate must be taken and processed

There are alloys which can be identified by the presence of one particular element. One grade of

Nitralloy containing over 1% aluminium is easily verified, with the added advantage that the test can be done even if the steel has been nitrogen-hardened.

Among the brasses, the complex type containing appreciable amounts of manganese and aluminium are easily distinguished from the straight copper-zinc alloys or naval brass. Among non-metallic samples, glass might be cited as a material whose type is easily placed by the spectrograph. A glance at one of the lead lines on the plate distinguishes between soda-glass and lead-glass.

(*c*). *Search for particular element or elements.* One example which comes to mind is a series of white paints for use under somewhat severe conditions with acid and sulphide fumes. The basis of these paints was TiO_2. Previous experience with this type of paint had shown that lead and zinc in any appreciable quantity were most objectionable. Later samples were spectrographed without any previous treatment, i.e., without removal of oil, etc., and from the plates it was a simple matter to say whether lead or zinc were present or virtually absent.

In the analysis of commercial copper, tin, zinc, lead, whether as ingot metal or manufactured as sheet, tube, etc., the analyst is concerned generally with less than 1% of total impurities. In the analysis, say, of ingot copper, if the spectrograph is not available, it is necessary to start up separate samples for estimation of many of the impurities tin, antimony, arsenic, bismuth, iron, etc., and much labour has to be expended whether these are present or not.

If the sample is arc-ed and the resulting plate examined in the Judd-Lewis Comparator, along with spectrograms of (*a*) pure copper, (*b*) copper containing all the probable impurities ; it is only the matter of a minute or two by reading the plate to see what type of copper the sample is. A glance will show, for example, whether arsenic is present in quantity and whether it is desirable to start up a chemical estimation.

(*d*). *Examination of very small samples.* A surprising number of cases arise where it is necessary, in order to piece together the mechanism of some occurrence, to have an approximate analysis of samples under 0·5 gramme in weight, sometimes under 0·1 gramme. In instances covering various types of corrosion and seizure, this was all that was available.

When a pump sent in for repair shows excessive erosion, it is sometimes possible to obtain small samples of deposits in odd corners or in thin layers over certain parts of the surface. Microscopic examination frequently shows sand grains, coke particles, fragments of glass and other foreign bodies. Thereafter, the spectrograph is used to indicate the elements present and thereby enable the best use to be made of the small remaining amount for chemical analysis on something approaching micro-analysis lines.

Quite often the information on the elements found is sufficient without further verification. Some tools with small tips apparently welded on were easily identified as having been stellited, by the presence of large amounts of cobalt and tungsten. It would be difficult to arrive at this information readily by other means since the tip is small, cannot be softened and drilled, and is fused on to the body of the tool.

The ability to take a spectrograph from a small area has proved useful in finding the reason for some of the hard spots found in castings. Recently, small hard inclusions in a gunmetal casting were identified as particles of ferro-manganese.

Quantitative Analysis

The methods of quantitative spectrographic analysis have already been fully described in various articles and papers to societies.

Generally the maximum amount of any one element estimated is about 4%, though spectrographic methods have been described for up to 20% of single elements in alloy steels. In these notes, however, the quantities concerned are seldom over 1%.

It is not proposed to describe the details of the technique here. It will suffice to say that the estimations referred to later are made by the "internal comparison" method. By means of the micro-photometer measurements are made of the relative intensities of a line of the minor element and a near-by line of the major element. Thus in estimating manganese in steel the density of manganese line 3442.0 A is compared with that of iron line 3443·9 A. The accuracy of the determination is thus not appreciably affected by slight unavoidable deviations from the standard conditions of exposure, plate characteristics, development, etc.

For quantitative work it is necessary to have as a basis a set of carefully analysed samples with graded amounts of the element to be estimated. If, as in the case of steels, data on the technique of exposure, development, etc., is available, it is only necessary to run through the set of standards on the operator's instrument to obtain the relevant log-ratio curves.

Estimation of Lead in Monel Metal

Although, as explained at the outset, the number of steels, etc., to be analysed in this Laboratory does not warrant the use of the spectrograph as an alternative to chemical analysis, there has been occasion to develop spectrographic practice for one or two alloys where ordinary chemical analysis is long and troublesome. In the author's foundry, Monel metal scrap arising from the machine shops is melted into ingots which are later remelted and used along with virgin metal for the production of castings. It was found some years ago that traces of leaded alloys found their way into the Monel metal scrap and that a very small lead content (about 0·06%) in Monel castings was sufficient to cause hot-cracking. The laboratory was faced with the need for analysing perhaps five heats per day for traces of lead. The accuracy required was of the order of 0·005% on amounts up to about 0·08%. By ordinary chemical means this is a tedious operation, calling for high operative skill and involving large samples which in turn require large amounts of acids to dissolve them. It was therefore resolved to prepare the necessary samples for spectrographic analysis and develop the log-ratio curve. A range of samples containing up to 0·1% lead was melted and carefully analysed. The Mond Nickel Company R. and D. Laboratory, Birmingham, kindly carried out check analyses and after some preliminary work the conditions for the estimation of lead were established. As a result, the estimation of lead in Monel metal samples is a relatively straightforward routine operation. Five samples can be run through in an overall time of under two hours. Incidentally, it might be added that this work, by the elimination of lead-bearing scrap, has resulted in the disappearance of cracking troubles.

Later, another set of similar alloys was made with lead and tin up to 1% each. From these curves were prepared and now chemical analysis for these two impurities is never found necessary.

Estimation of Magnesium in Nickel-Copper Alloys

These alloys contain Mn, Fe, Si, up to 3% Al and up to 10% Sn, so the chemical estimation of magnesium is by no means easy. Magnesium is the usual deoxidiser, and is added in quantities from 0·06 to 0·1%.

It was decided to make a study of the effectiveness of these additions, the rate of loss after addition, the effect of remelting, etc., and before this could be undertaken it was most desirable to be able to carry out magnesium determinations in considerable numbers, and with a high degree of accuracy.

The experimental work was done on a set of seven analysed samples containing 0·003 to 0·170% of magnesium, obtained from U.S.A., through the kind help of Dr. Griffiths of the Mond Nickel Company, London.

After the conditions for exposure had been settled, it was found that the very first log-ratio curve ran smoothly through all the points, a tribute to the accuracy of the analyses.

The spectrograph was then put into regular service for the determination of magnesium in a large number of casts. The data thus given went a long way towards appreciation of the function and behaviour of magnesium. An apparent discrepancy in some samples taken from the same cast led to some interesting findings on the flotation of magnesium. This was verified by very slow cooling of some ingots which were later sectioned. Sulphur prints and subsequently combustion sulphur estimations, combined with magnesium determinations and microscopic examination, give a much clearer idea than had hitherto been possible of the interaction of Mg, Mn, S and O_2 in the conditioning of these alloys.

The foregoing examples have been given at some length in order to indicate the value accruing from the greater ease and probably greater accuracy given by the spectrograph in determination of trace elements.

It will be appreciated that many similar estimations can be done, if the need arises, even if no previous guidance is available, and the operator has therefore to make or obtain his own standards and work out his own curves.

Approximate Quantitative Analysis

A simpler method can be utilised for certain analysis where several minor impurities have to be estimated. In brasses, as many as nine elements may have to be searched for. The preparation of the various series of graded analysed samples and the development of log-ratio curves for these would be laborious. Results sufficiently accurate for checking against specification limits are given by visual examination. Data is available in the form of tables for impurities in brasses, steels, lead-alloys, etc. The following table, from a recent paper by Milbourn[1] is typical :—

VISUAL ESTIMATION OF ARSENIC IN COPPER-RICH ALLOYS.

Arsenic 0·003%	As 2349·8 A	=	Cu 2363·2
0·02 %	As 2860·5 A	=	Cu 2862·0
0·04 %	As 2860·4 A	=	Cu 2851·8
0·1 %	As 2860·4 A	=	Cu 2858·7
0·2 %	As 2860·5 A	=	Cu 2858·2
0·4 %	As 2898·7 A	=	Cu 2911·2.

In order to apply these comparisons it is necessary that the whole procedure for obtaining the plate should be in exact accordance with the details given by the authors of the data.

Obviously it is a matter of chance whether a sufficient number of suitable lines of the minor element exist and whether comparable lines of the major element are also to be found in the vicinity on the plate. This visual comparison depends on the operator, but tests show that several operators reading the same plate arrive surprisingly close to agreement. The method is most accurate at low percentages of the minor element, i.e., when the lines are not very dense. The visual estimation is helpful in the analysis of gunmetal purchased against emergency specifications such as B.S. 1023/4. At present gunmetals have to be made with much more scrap than in normal times and the percentages of impurities, arsenic, antimony, aluminium, etc., are liable to be higher than would ordinarily be encountered. These can all be estimated spectrographically at the expense of very little time and a low cost and the information thus provided can prevent intrusion of further foundry difficulties.

Miscellaneous Investigations

Practically all the foregoing applies to work which can be done, if absolutely necessary, by chemical analysis. A few examples will be given of applications where the spectrograph offers unique advantages. These are taken from cases of corrosion, seizure, and season cracking.

Corrosion

Here the spectrograph is partially a substitute for micro-analysis with the added advantage, however, that the results can be obtained in cases where it is next to impossible to detach the sample from its surroundings. An example might be given from the case of a steel boiler tube showing what has been termed "scab pitting." Under the detritus in the affected areas there was evidence of metallic copper at the bottom of the holes. This copper had been deposited slowly and was very firmly adherent. Using the method described by Barker, Convey and Oldfield[2] and employing a silver electrode, a series of spectrograms was taken on the normal tube surface and over various parts in the pitted hole. The spectrographic analysis disclosed not only varying amounts of copper but local concentrations of both silicon and manganese. This is an instance where it is difficult to imagine any other method of obtaining the information since the areas tested were perhaps $\frac{1}{16}$ in. diameter and were very close to each other.

Seizure

The same technique for examining very small samples has been applied to some cases of seizure. In one instance, recently, a fragment of a foreign body had found its way between the two faces of a slide valve in a machine on test and had caused tearing. The fragment, no more than $\frac{1}{16}$ in. diameter, was firmly embedded in one of the surfaces. In taking the plate, the adjacent metal was also sparked and it was determined that the foreign matter was cast iron. Further exposures were made under the standard conditions used for cast iron analyses and it was possible to give the silicon, manganese and nickel contents.

Season-Cracking

A rather unusual application of the spectrograph arose in a case of season cracking of a brass casting. The failure occurred in a location where ammonia was unlikely to be present and traces of mercury were suspected. Spectrograms were taken from the fractured surface and also from an unaffected part of the casting. On the same plate adjacent spectrograms were taken of a pure mercury salt by means of the Hartmann diaphragm. The results were so clear that they could be readily understood by persons having no experience whatever of the spectrograph. The spectrogram of the fractured surface showed a distinct mercury line in exactly the same position as in the pure mercury salt, whereas the spectrogram of the unaffected casting showed no line at the mercury wavelength. It might be added that in this case the possibility of mercury vapour in the plant was afterwards verified.

Non-Destructive Testing

Spectrographic examination can be said to be an addition to the means at our disposal of non-destructive testing and it can be readily understood that it is a matter of considerable importance occasionally to be able to derive the desired information without softening and drilling a piece of material. During the war occasions have arisen where it has been necessary to duplicate an existing part without damaging the original. This has applied to small but important components of machinery of naval vessels belonging to allied nations in which case no information was available of the material and treatment. The spectrograph readily identifies the type of material, generally steel, and from the Vickers hardness figure and the knowledge of the duty of the part, it has been a fairly simple matter to produce a suitable equivalent.

Reactions in Chemical Laboratory

In the chemical laboratory itself the introduction of spectrographic equipment can be made to effect a noticeable improvement in general technique and results. This is occasioned in several ways.

(1). By the intelligent use of qualitative spectrographic results giving a rough approximation of the element studied, the most suitable method and quantity of sample can be chosen.

(2). The purity or otherwise of precipitates is readily established. Suppose in an analysis a small quantity of precipitate is obtained which is presumed to be Al_2O_3. It is difficult with chemical means but easy with the spectrograph to check whether such a precipitate is pure or if it contains say SiO_2 or TiO_2.

(3). The analysis of standards for log-ratio curves calls for the highest possible standard of accuracy. If, in the preparation of a curve, one point does not lie reasonably near the mean line, the analysis is questioned and it has generally been found that the analysis has been at fault. In the laboratories where both chemical and spectrographic methods are used and checked against each other, it is reported that there has been a general tightening up of analytical procedure and useful questioning of methods.

Here, it might be added that the use of the spectrograph for the miscellaneous purposes indicated will generally involve no cost except the operator's time. In even a small laboratory, at least one plate (pre-war cost 10d.) will be exposed each day. Up to thirty spectrograms can be taken on one plate and unless there is a fairly large amount of routine work to be done, there will be space to spare.

General

The significance of much of the preceding matter may be appreciated if we consider the trend of metallic alloys in the last two decades and the prospects of the future. A very large number of the less common elements are now being used in alloys, and the percentages are nearly always low. In the steel group we have Ti, Cb, Zr, B, Pb, in the lead alloys Te, in the light alloys Ti, Ce, Na, and in the copper and nickel base alloys Be, Ca, Ba and Li. This trend is adding to the complexity of the analyst's task.

In chemical analysis there is a noticeable inequality in the response of the various elements. The chemist's life would be much easier if each element gave a precise exclusive precipitate, preferably coloured and of a texture well suited to filtering media. Nickel, with its glyoxime reaction, is a pleasant example.

Unfortunately many elements are unsatisfactory from the analyst's point of view. Some elements such as boron are elusive in that they do not readily give us useful precipitates. Many elements give us group rather than specific reactions and separations depend on the careful attainment of precise conditions of temperature, pH, etc.

The spectrograph is no respector of elements because although the number of lines differs enormously from element to element, the lines do show up if the element is present. If one is searching for a rather unusual element its presence can be positively recognised by comparison with a pure salt of the element using the Hartmann diaphragm.

Admittedly, much of this paper has been written largely from the point of view of the user of analytical results. Nearly all the analyses coming into this laboratory are done for a specific object and in consequence the significance of the results is known. This means that the laboratory is not called upon to produce complete analysis of every sample in the manner of a public analyst's establishment. There is little doubt that many estimations are done quite needlessly, for example, in many alloy steels silicon and manganese are estimated as a matter of ordinary routine. The results concern the maker of the steel much more than the user. By paring down complete analysis to the essential elements, especially in a small laboratory, manpower can be freed for vital estimations.

It is unfortunate that the plant required in spectrography is costly. This is the more noticeable because ordinary chemical analysis involves so little capital outlay. The biggest proportion of analyses in an engineering laboratory can be carried out with a balance, a muffle furnace and a variety of simple glass-ware. To these may be added a combustion furnace for carbons and an electrolytic set-up for copper alloys but the whole cost for plant is small.

This simple apparatus, however, only yields results in the hands of operatives of a high degree of skill and ingenuity. There are probably no two elements whose chemical estimation is carried out in exactly similar fashion and the method of estimation of any one element has to be varied to suit the material which is being tested. A method for the estimation of manganese in

mild steel may be quite unsuitable for the same estimation in stainless steel for the simple reason that the latter is not soluble in nitric acid.

Spectrography calls rather for precision and careful adherence to a standardised procedure. The six unit operations :—preparation of specimen, excitation, exposure, development, density measurement, and conversion to percentage, are simple in themselves and it does not require a long time for a person of good general education and the aptitude for neat manipulation to produce reliable results when working on estimations which have already been established. The work involved in tackling something new calls for skill and experience of a similar order to that required for evolving a new method in chemical analysis.

(1) "The Spectrographic Analysis of Copper and Copper-Rich Alloys by the Arc Method." Maurice Milbourn, B.Sc., A.R.C.S. Institute of Metals. Vol. 69. Part 10, 1943.
(2) "The Application of Spectrographic Methods to the Analysis of Segregates." F. G. Barker, F.I.C., J. Convey, Ph.D., and J. H. Oldfield.

Conclusion

To the writer, it is clear that physical and optical methods have already many worth-while applications in a general laboratory. The two approaches which we might call crudely the chemical and the physical are best regarded as supplementary. We meet problems where chemical methods are long and laborious and some where they are just not good enough ; it is in these cases that it is wise to enquire if any physical approach is possible.

Acknowledgements

The writer wishes to acknowledge the excellent work of Mr. James McPheat and Mr. F. B. Ling who have put the spectrograph to the varied uses outlined above.

Finally, the writer is indebted to the directors of G. & J. Weir, Ltd., for their interest in this and many other scientific developments and for permission to publish this note.

Cheap High-Duty Steels

By J. Edmiston

As a result of experience under war-time conditions, it is probable that the future trend in steelmaking will be production to physical properties, rather than to chemical specification, and attention will be given to the possibilities and limitations of the most economical types of alloy. In this way the " residuals " in war-scrap can be used with advantage in the production of high-duty alloy steels economically.

ONE good result of the present war, so far as the steel industry is concerned, is that greater attention is now paid to efficiency, both in the manufacture of steel and the performance of the product in service. As in other industries, force of circumstances led to the adoption of many substitutes. Happily, most of these substitutes proved to be much better than was at first thought possible. The new steel specifications are no exception, and a great many appear destined to have a permanent place in the engineering world. Indeed, it is now clear that many pre-war specifications were really extravagant in the use of valuable alloying material for most of their applications. Possibly this arose from the use of excessive factors of safety. This cautious attitude of engineers certainly discouraged experiment with new materials. Whatever the real reason may be, recent experience has focused attention once more on the virtues of the lower-alloy types of steels.

Now that engineers are in a more receptive mood to change an excellent opportunity arises for the industry to explore and map out the boundaries of this new territory ; in other words, to examine the possibilities and limitations of the more economical types of alloy. In this way it will be possible to make the most of the " residuals," copper, nickel, and molybdenum, which are bound to appear in considerable amount when war scrap returns to the furnaces. At present, these elements are often ignored since it is uneconomic to attempt their elimination. A more logical and economically sound method of dealing with them is undoubtedly to take advantage of their presence by suitable additions to build up high-duty alloys.

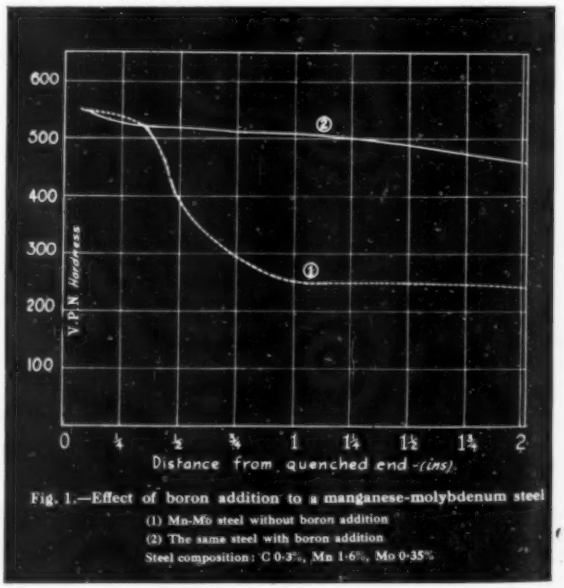

Fig. 1.—Effect of boron addition to a manganese-molybdenum steel
(1) Mn-Mo steel without boron addition
(2) The same steel with boron addition
Steel composition: C 0·3%, Mn 1·6%, Mo 0·35%

A good deal of work has already been done on these lines in the United States. There the " N.E." series of steels, all of low alloy content, compare very favourably in properties with the more conservative British "En" series. Even so, the present tendency is for the "En" types to follow the American system. Recent American

research on the various factors affecting "hardenability" show that chemical composition as revealed in ordinary testing routine may not be of great value in assessing the merits of one alloy over another. Hardenability, and of course, the ultimate physical properties of the steel, can be very profoundly influenced by minute percentages of such elements as aluminium, titanium and boron. There seems to be little doubt that the action of these elements is mainly physical, influencing as they do, grain size and depth of hardening. Close control at the melting stage is therefore of primary importance.

The future trend of steel making is likely to be production, not to chemical specification, but to physical properties, which involves control of hardenability. The real criterion as to the suitability of a given steel for a specific purpose will be some test which involves measurement of this rather elusive quality. So far, the Jominy test, in spite of its imperfections, is the most successful in this field; at all events it is easily the simplest and quickest to perform and will probably remain standard for some time to come. Whatever test becomes standardised for specification purposes, it will certainly become necessary for the steel industry to put in hand researches to determine practical limits within which commercial production can operate. Such problems as the heat-to-heat variations encountered in a large number of similar charges, the precise effect of small additions of "controlling" elements on hardenability and probably many other less well defined investigations arising from actual practice, will require attention. It might be objected that this is merely statistical work of no immediate urgency, but if this country wishes to take its place as an exporting steel producer after the war, a large background of experience in cheap alloy steel will obviously be necessary, and the accumulation of statistics is the surest way to acquire it.

Once the engineer appreciates the full implications of the term "hardenability," the manner in which this method of specification might work out in practice can be roughly outlined. Minimum tensile and elongation might be desired on, say, a 2 in. section, leaving the choice of the steel to the discretion of the steelmaker. Again, a particular type of steel might be called for and a Jominy range specified, leaving the "controlling" elements to the choice of the manufacturer, or even a composition and maximum hardenability only quoted. A little reflection will show that each of these methods have their uses. Faced with this problem, the steelmaker, armed with the necessary statistics, will be able to compete on a basis of cheapness and ability to meet specification.

Turning now to the practical aspects of these new lines of development, it is interesting to examine present-day trends. The Jominy test is not of such "hair-splitting" accuracy that undue attention or weight should be placed on slight variations revealed from cast to cast by any particular class of steel. Nevertheless, the Jominy test can easily separate types showing abnormal hardenability, such as can be induced by the "controlling" elements previously mentioned. This is made clear in Fig. 1. where typical curve ranges of manganese-molybdenum steels of both normal and specially treated casts are shown. In this case, the hardenability characteristics are clearly separated by the marked dis-similarity in shape of the two curves. In general, all the low alloy steels can be made to yield similar pairs of curves, in a greater or less degree, according to their composition. There is thus no need for the steelmaker to carry extensive stocks of each specification segregated into a large number of batches of varying hardenability. For all practical purposes, two varieties of each specification, a representative of the upper group and a representative of the lower group, would be likely to meet every possible demand.

The probable field of usefulness for these low alloy types of steel is not entirely confined to those showing maximum hardenability in each specification. There are cases which arise in practice where deep-hardening properties might be undesirable; for example in welding assemblies, where even slight self-hardening properties might lead to cracking. Here, practical experience can help in defining the best working limits for any particular design. The other extreme could be imagined in applications where it is desired to maintain impact strength and hardness by lowering the carbon, taking advantage of boron as a hardener in preference to other more orthodox alloys.

In the United States, as much as 0·5% nickel is met with as a residual in ordinary melting, even now. Frequently, 0·2% molybdenum also occurs, so that little additional alloy need be added. These residuals are usually made up of "N.E." types with the addition of chromium, and boron now appears to be freely used. In this way, advantage is taken of a "present" of valuable alloys which are almost constant constituents of the scrap. It does not require a prophetic gift to visualise a time, in the near future, when British steelmakers will be faced with very similar conditions.

With the future emphasis on the properties of the finished product and less stress laid on mere chemical composition, an opportunity will occur to explore the possibilities of unusual alloy combinations. Complex alloys of the copper-nickel-molybdenum and nickel-manganese-molybdenum steels, for example, could certainly be developed commercially as cheap medium-tonnage structural steels. In this way, it is suggested, the British steel industry will be most likely to meet competitors on equal terms in the export markets of the world.

Of course, the full exploitation of these steels demands modern melting methods. Manganese (a valuable alloy), is often entirely lost to the slag in the ordinary way, even in the basic open-hearth process. In the "dead-melting" technique of the basic electric furnace, manganese loss could be entirely eliminated. The use of high manganese with low nickel and molybdenum is indeed one very promising avenue of future development for the electric furnace. In spite of its drawbacks, the basic open-hearth furnace can at least keep manganese loss down to a minimum, although naturally, such elements as chromium would still be lost. Consequently, if chromium were also desired the electric process would be preferred. Thus, it will be readily appreciated, the ideal plant for this type of output would be sufficiently flexible to take advantage of whatever scrap happened to be available in order to produce the required grade of steel with the least expensive additions. For example, "armament" scrap alone would require little refining, and dead-melting practice could be advantageously followed. Very mixed scrap, of unknown origin for the most part, would require some preliminary refining, and a certain loss of some alloy would have to be accepted.

The Tankdozer

AMONG the large number of developments the needs of the war have fostered not the least important is the tankdozer which, during recent months, has occasionally been mentioned in the daily Press. According to information, recently revealed in some detail, the tankdozer is a medium Sherman tank mounted with a bulldozer blade. It is equvalent in work capacity to the heavy tractor dozer, commonly known as the bulldozer, which is universally used for earthmoving operations in construction. A hydraulic jack, which receives power from a pump in the tank driven from the tank engine, is used to operate the dozer blade. Bulldozing operations may be accomplished with the tank driver "buttoned up." The fire-power of the tank is not reduced. A quick-release mechanism actuated from within the tank allows the bulldozer blade assemble to be jettisoned in about 10 seconds, freeing the tank for fighting purposes. Thus are combined in one instrument a tank with its fighting ability and a bulldozer with its construction ability.

The tank-mounted bulldozer blade was developed by the Corps of Engineers in co-operation with manufacturers. The idea was originally formulated as early as 1940, but the evolution of the idea did not take concrete form until 1942. By June, 1943, the first pilot model of the tankdozer was completed and there followed a series of service tests which resulted in the final design. Quantity production began in December, 1943.

The tankdozer is applicable to any requirement for bulldozer power, tank fire power and personnel protection. In the assault of obstacles the vehicle will overcome anti-personnel obstacles such as barbed wire entanglements and anti-personnel mines ; anti-mechanised obstacles such as log cribs, log posts, road craters, anti-tank ditches, concrete cubes, steel tetrahedrons, hedgehogs and anti-tank walls ; it will reduce bunkers or pillboxes by covering over or destroying them ; and it is well adapted to emergency engineer construction operations such as construction of jungle trails in the face of enemy sniper fire, construction of by-passes under fire and the preparation of emergency stream crossings in the face of the enemy.

In general, the tankdozer has three fundamental strengths ; fire power of the tank unimpaired by the bulldozer blade ; an ability to move earth comparable to that of a heavy tractor dozer, and great weight and momentum. The combination of these features results in incomparable destructive ability. It breaks through obstacles either by the impact of brute force or by moving earth to build ramps over or past the obstacles.

This new weapon has been used in Normandy to break through the hedgerows and lead the way for mechanised weapons. In combat in Italy the tankdozer was used to fill bomb craters in roads, to push disabled vehicles off the road, to construct by-passes around blown bridges, to dig in half-tracks and other vehicles in forward positions within enemy shelling distance, to construct fills over newly-installed culverts, to cut through railroad embankments for new roads to replace demolished highway overpasses, to clean out rubble in towns at points blocking traffic, and to fire with the 75mm. gun and 0·50 calibre machine-gun on enemy anti-tank positions and machine-gun nests.

Micro-Analysis in Industry

AT a combined meeting of the South Yorkshire Branch of the Royal Institute of Chemistry and the Sheffield Metallurgical Association which was held in Sheffield on Friday, 13th October, Mr. R. Belcher, F.R.C.I., gave an address on Industrial Applications of Microchemical Analysis. Mr. Belcher stressed that misunderstanding of the object of developing such methods was very prevalent. Microchemical methods should not be devised in order to supplant existing macro-methods, but in order to supplement them. For example, where samples are limited in amount or expensive, or where dangerous substances are being dealt with, there is every justification for micro-methods, since macro-methods would be either impossible or inadvisable.

In fuel analysis, small coal dust or mine dust samples often require analysis, and methods have been devised for this purpose. The determination of ash, elements, calorific value and moisture were described in this connection.

Metallurgical analysis and the analysis of explosives and of rubber are other spheres in which micro-methods have managed to solve problems more easily or more satisfactorily than would have been possible on a larger scale.

Exhibition of Apparatus

On the following day, under the same auspices, a demonstration of microchemical apparatus and technique was held at Rotherham Technical College. Examples of procedures in qualitative organic and inorganic analysis were carried out by students who had been trained in the microchemical courses organised by Mr. Belcher at the College. The latter included several varied types of group separations. The electrograph, fluorescent indicators, the Emich method for determining boiling points, using Morton and Mahoney's optical system, the polarograph, and the "magic eye" as applied to electrometric titrations were also displayed in operation. Examples of organic and inorganic chromatograms were included, and several pieces of apparatus loaned by Messrs. Griffin and Tatlock, Ltd., including the Elekhardt micro-acetyl apparatus and the Kirk apparatus for ammonia distillation, were also on show.

One interesting exhibit was composed of pieces of apparatus with various applications in qualitative inorganic micro-analysis, which had been made during their course by students of the College.

Education in Microchemistry

During the morning, three short talks on "Some Aspects of Microchemical Instruction" were given by Dr. Cecil L. Wilson. In his first talk Dr. Wilson stressed that carefulness and initiative were developed in students using the newer techniques. His second talk showed that with microchemical methods there could be considerable saving in materials, apparatus, time and space. Finally, Dr. Wilson suggested and outlined three necessary types of microchemical course : broadly educative ones for more junior students or for those unfamiliar with the field ; specialist courses in established branches ; and advanced courses dealing with the less known, or more recently developed microchemical techniques.

Both the evening meeting and the Saturday exhibition were attended by large audiences, who, by their interest, showed their appreciation of the highly commendable initiative of the sponsors of the two meetings.

The Influence of Melting Conditions on the Physical Properties of Steel Castings

By H. T. Protheroe, B.Sc.
(*The University of Sheffield*).

A detailed report of an investigation on the mechanical test results obtained from a number of cast steels from various sources is given in a recent paper published by The Iron and Steel Institute A critical examination of the data recorded during manufacture has been made and used in connection with mechancial test results in an effort to trace the factor or factors having the most pro nounced influence on the quality of cast steel. The report is presented here in a substantially abridged form.*

THE object of this investigation was to determine, as far as possible, the factor or factors which, during the various steps in the production of a steel casting, had the most decided influence on the mechanical properties of the final product.

Forty-eight test pieces were made under various conditions of manufacture, each heat provided three clover-leaf test bars from which the subsequent mechanical test-pieces, micro- and macro-specimens, etc., were obtained. The method of cutting the test pieces is shown in Fig. 1.

For each heat all the available data, such as the method of manufacture, melting and casting temperatures, final deoxidation additions, etc., were recorded. The steels were tested in the as-cast, the annealed and the normalised and tempered conditions, each test being done in duplication. Every steel was examined microscopically and photographed in all three conditions, as follows :—

1. Polished ; unetched. ×50.
2. As cast ; etched. ×50 ; ×500.
3. Annealed; etched. ×50 ; ×500.
4. Normalised and tempered ; etched. ×50 ; ×500.

In addition, a macro-etching of the cross section of one clover-leaf test-piece from each heat was examined and photographed. In all, 432 test pieces were prepared and tested, 192 micro-specimens were cut and polished and 366 photographs were taken and 48 macro-etchings were prepared and photographed.

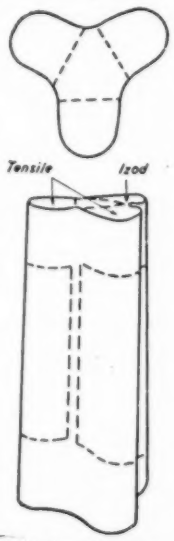

Fig. 1.—Clover-leaf test bar ; method of cutting into test pieces.

Mechanical Tests

The results of the mechanical tests together with the data concerning the melting conditions, process, etc., are tabulated. This table includes a column which indicates the condition of the test-piece. Those test-pieces which machining revealed to be unsound are indicated as being "blown." Other test-pieces were not obviously blown, but contained regions of intercrystalline porosity which were obvious only after fracture or became revealing during the pulling of the test-piece by the appearance of a very minute hole in the originally sound test-piece ; these are indicated as being porous.

Whatever the factor or factors having the most decided influence on the mechancial properties, no indication is gained by even a very close examination of the data tabulated. Unsoundness, as indicated by either blow-holes or porosity, in many instances might reasonably account for the inferiority in the mechanical results ; obviously, unsoundness must have a pronounced effect, but it is the sole contributing factor to variations in the results

Considering the steels as a whole, without taking into consideration any variation whatever, the first and perhaps only noticeable fact is that that maximum stress seems to be the most constant measure of quality—in other words, the property which seems to be least affected by variations in the deoxidation method or process, or by the influence of any factors, whatever they might be, is the maximum stress.

A graphical representation of the results as shown in Fig. 2 (*a*) only confirms existing knowledge, viz., that an increase in maximum stress is expected with an increase in carbon content. With so many factors having even only a slight effect, the nature of which cannot be definitely stated, graphical representation of results indicate definite trends rather than any absolute relationship. When the steels are arranged according to their carbon contents the average maximum stress figures in Table II are obtained. These show a gradual increase in maximum stress with increasing carbon content.

TABLE II.
INCREASE IN MAXIMUM STRESS WITH INCREASE IN CARBON CONTENT.

Group	Carbon, %	Number of Steels	Max Stress (Average), Tons per sq. in.		
			As Cast	Annealed.	Normalised and Tempered.
A	Below 0·2	5	29·2	29·5	31·0
B	0·20–0·23	16	31·3	30·9	31·8
C	0·24–0·26	21	35·8	33·4	33·7
D	Over 0·26	6	35·6	34·0	35·3

* Paper No. 11, 1944, of the Steel Castings Research Committee (submitted by Professor J. H. Andrews, D.Sc.). Published by the Iron and Steel Institute, Aug., 1944 (Advance Copy).

The results of the annealed and the normalised and tempered conditions are shown graphically in Figs. 2 (*b*) and 2 (*c*). Other elements like sulphur and phosphorus are not expected to affect the maximum stress so much as the reduction of area and elongation. What little effect is imparted by nickel and chromium may be annulled by the greater influence of other factors, and it is probably for this reason that any attempt to determine the effect of nickel, chromium or manganese prove unsatisfactory.

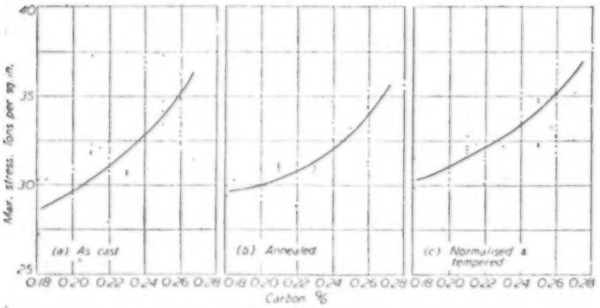

Fig. 2.—Effect of carbon content on the maximum stress

The maximum stress, because of its only slight variation in value from one steel to another, which variation can be attributed quite legitimately to variations in composition only, will not give much indication of the quality of the different steels. A better criterion of quality will probably be the impact value, the reduction of area or the elongation.

For this purpose the steels are again grouped and tabulated according to their carbon contents. In one group (carbon 0·20–0·23%) for a maximum stress of 31 tons per sq. in. an Izod value of 14 ft. lb. can reasonably be expected. The figures given are the averages after ignoring abnormally high values or abnormally low ones due to obvious defects. Over this small range of composition it is reasonable to assume that the Izod figure is inversely proportional to the maximum stress. Thus, by using the ratio of the maximum stress to the Izod value given by the average figures the expected Izod value for any maximum stress can be calculated. After this adjustment for tenacity, the Izod figure obtained on actual test will be a measure of its quality, the latter being expressed as a positive or negative value, i.e., the difference between the expected and actual results. Those steels with a minus value of more than 4 are classified as inferior, those between −4 and +4 as normal and those with a greater value than +4 as superior.

Tabulating the steels according to quality in this way, of ten steels classified as inferior, seven are inferior in all conditions, i.e., whether as cast, annealed or normalised and tempered. It appears, therefore, that the factor influencing the as-cast quality persists after heat-treatment. In an attempt to determine this factor, all the steels were grouped according to their quality and all relevant data, like conditions of test piece, sulphur and phosphorus contents, casting temperature, deoxidation method, etc., were included. This revealed that all the steels with a combined sulphur and phosphorus content of over 0·09% are inferior in all conditions, and those with a low combined sulphur and phosphorus content that are inferior show signs of unsoundness either as blow-holes or as porosity.

The influence of the combined sulphur and phosphorus content on the Izod value is shown graphically in Figs. 3 and 4, where the impact values are plotted against the total sulphur and phosphorus. The steels are grouped according to their carbon content.

Classification of the steels according to their reduction area or elongation gives similar results as when using the Izod value except that a larger number of steels are classified as inferior in each case. It was noted, however, that unsoundness has a much greater influence on

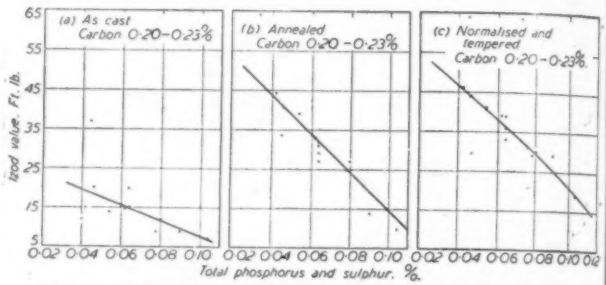

Fig. 3.—Influence of combined sulphur and phosphorus content on the impact value of steels containing 0·20–0·23% carbon.

the elongation and reduction of area. The influence of the combined sulphur and phosphorus content is graphically shown in Fig. 5.

The wider scattering of the points both for elongation and for the reduction of area in Fig. 5 (*a*) is probably due to two causes: First, there is an "as-cast" factor exerting a slight influence, which is relieved to a certain extent by annealing or normalising and tempering, probably the internal stresses common to as-cast metals; and secondly, the stronger influence of unsoundness on the reduction of area and elongation than on the Izod value.

Deoxidation Method

With the exception of about six steels, all those examined were given one of three final deoxidation treatments. One group was deoxidised by the addition of 6 oz. and a second 24 oz. of aluminium per ton; to a third group 8 oz. of calcium-silicon-manganese per ton was used. These treatments were final deoxidations and were additional to the general or bath deoxidation technique as practiced by each manufacturer.

To determine whether the final deoxidation method had any effect on the mechanical properties 42 steels were divided into three groups, according to the method of deoxidation. A comparison of the test figures does not enable any convincing statement to be made regarding the effect of the deoxidation method. The differences in value of any particular test, with the exception of the impact, are too small to indicate that one method is better than another, particularly in the as-cast condition; in both the annealed and the normalised and tempered conditions, however, there is a definite indication that the addition of 24 oz. of aluminium per ton gives better impact values than either of the other methods used.

It is not expected, however, that final ladle deoxidation would have a pronounced effect on the quality of the steel. What is far more important is the general bath deoxidation technique. Additions of 6 to 24 oz. of aluminium per ton of steel will not have the same effect on a badly oxidised steel as on one completely deoxidised.

Inclusions

Closely allied with the deoxidation technique is the nature and disposition of the non-metallic inclusions. Every steel was examined in the as-cast condition, polished and unetched, to obtain information on the distribution of the inclusions. Microphotographs of the

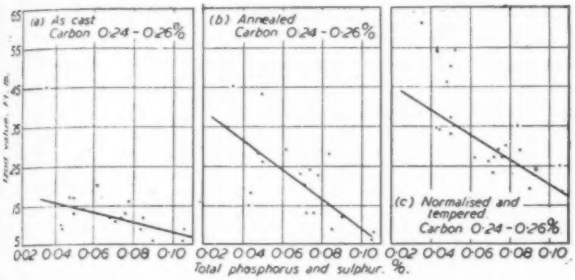

Fig. 4.—Influence of combined sulphur and phosphorus content on the impact value of steels containing 0·20-0·23% carbon.

unetched specimens were taken at a magnification of 50 and revealed two distinct types, viz., inclusions randomly distributed and those distributed around the grain boundaries. No definite reasons for these different forms of inclusions are evident from the data providep.

The melting, tapping and casting temperatures do not appear to influence the distribution. All casting temperatures, with six exceptions, were measured with an optical pyrometer. Steels cast at temperatures from 1385° to 1500° C. have the grain boundary type of inclusions, but quite a number cast at the same temperature show the random type. Similar remarks apply to the melting temperatures. What will determine the distribution of the inclusions is not the melting or casting temperatures of the steel but the composition and solidification temperature of the inclusions themselves. If they are of a low melting point they remain molten after the commencement of solidification of the steel itself, and, being the last constituent to solidify, they will be located in the grain boundaries of the steel. The only factor which will determine the actual melting point of the inclusion is their composition, and this depends on the chemical reactions occurring in the bath of steel during manufacture and as a result of the general deoxidation technique.

An examination of the data regarding slags and general deoxidation technique failed to provide any indication of what to anticipate with regard to the nature of the inclusions in the final steel. Actually, this is to be expected, because no data are provided with respect to the temperature of the bath when the additions of such ingredients as lime, ferro-manganese, ferro-silicon, etc., were made, or the time for which the various reactants were in contact—two only of the various factors which must have some effect on the final products of reaction.

There is no connection between the percentage of non-metallics such as sulphur and phosphorus, elements like manganese in the final steel and the type of inclusions obtained. It is significant, however, that all the steels classified as inferior in all conditions are included in the group with grain-boundary inclusions with the exception of two steels, both of which are badly blown. What, then, is the deciding factor—the total sulphur and that, so far as impact values are concerned, the total phosphorus percentage or grain-boundary inclusions? Considering those steels which are sound and have grain-boundary inclusions, it is found that they give normal or superior results despite their grain-boundary inclusions. Their total sulphur and phosphorus content, however, is relatively low. It appears, therefore, sulphur and phosphorus content has a greater influence

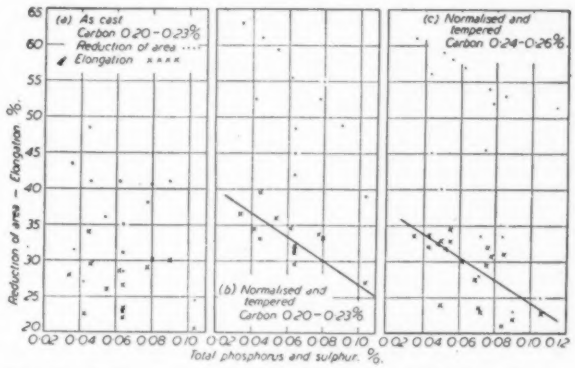

Fig. 5.—Influence of combined sulphur and phosphorus content on the reduction of area and elongation.

than the nature of the inclusions. Similar conclusions are arrved at when the reduction of area and the elongation are considered in the same manner.

Effect of Various Temperatures

All attempts to correlate the mechanical properties with tapping temperatures, ladle temperatures or casting temperatures met with no success. It is probably true to say that the influence of other factors is far more pronounced and annuls any influence that these temperatures may have.

A series was specially prepared to investigate any effect that melting or casting temperatures might have when the influence of other factors like the bath and final deoxidation, process of manufacture, composition, etc., is eliminated as far as possible. Six tests were obtained from three heats. The steel was made in an acid high-frequency furnace and the maximum temperature recorded was a little over 1690° C. Test bars were cast from the same ladle of metal at suitable intervals, giving a range of casting temperature from 1500° to 1620° C. and the temperatures were taken with an immersion pyrometer. From the results of mechanical tests, the yield point and maximum stress do not appear to be affected by the casting temperature in the as-cast, the annealed or the normalised and tempered condition. The ductility, as measured by the reduction of area and elongation, is at a maximum in all conditions with a casting temperature of 1580° C. In the annealed and normalised and tempered conditions, however, the differences in the reduction of area and elongation between test bars cast at 1580° and 1620° C. are too small to be decisive. With regard to the impact values, except in the as-cast condition, the higher casting temperature gives the best results.

Grain Size

Graphs plotting the various temperatures, compositions, etc., against grain size do not indicate what the important factor controlling grain size is except the aluminium addition, which is the accepted medium for grain size control. The finer grained steels are those

which were deoxidised with 24 oz. of aluminium per ton. Some exceptions are noted, but no reason for these exceptions is apparent from the data. The mere addition of aluminium, without paying attention to the deoxidation technique, temperature, etc., does not produce a predetermined grain size. The grain-refining influence of aluminium has its effect on the mechanical properties, particularly on the impact value.

Hot-Etched Structure

Cross sections of the clover-leaf test bars were polished and etched from 20 min. in a boiling solution of 50% hydrochloric acid. Three typical examples of the resulting macrostructures show (*a*) A coarse columnar structure ; (*b*) a fine columnar structure ; and (*c*) a featureless structure. Why steels of practically the same composition should solidify in such different and distinct patterns is not readily apparent. From what is known about the mode of solidification of steel, the final macrostructure is controlled principally by the temperature gradients existing in the steel at the moment of commencement of solidification. A steep temperature gradient would induce a columnar structure, while a flat temperature gradient would indicate a more uniform rate of cooling from the inside to the outside of the mass of metal and hence give an equi-axed structure. The principal factors determining the temperature gradient are the conductivity of the mould material, the mass of the molten metal and the casting temperature. An alteration to any one factor can upset the influence of the other two. The influence of the casting temperature for example, is unpredictable without a specific knowledge of the conductivity of the mould ; nor does a high casting temperature necessarily mean a steep temperature gradient or a rapid non-uniform rate of cooling. For a given mass of steel, the higher the casting temperature, the greater is the quantity of heat to be absorbed and dissipated by the mould material. Moulding sands are notoriously bad conductors of heat, which, therefore, is not dissipated to the atmosphere but is accumulated in the mass of steel itself. This tends to flatten the temperature gradient and give a more uniform rate of cooling. Thus an equi-axed structure is quite possible even with a high casting temperature. With a somewhat lower casting temperature the heat may be dissipated at a sufficient rate to set up a more or less steep temperature gradient in the mass, thus producing a columnar structure. With very low casting temperatures only an equi-axed structure is possible.

The degree of coarseness of the structure, whether columnar or equi-axed, is determined by the rate of nucleus formation compared with the rate of crystal growth, the rate of nucleus formation in turn being dependent upon many factors, e.g., turbulence, presence of solid matter, temperature, etc.

From the data given in this investigation in support of these theories there is an indication that the majority of steels cast at temperatures above 1450° C. (optical) have a columnar structure, while at least six, also cast above 1450° C. have an equi-axed structure. With one exception, no steel cast below 1450° C. shows a columnar structure. A further indication of the effect of casting temperature is given from an examination of one series of the steels. Four were made from the same melt and therefore of the same composition, melted at the same temperature, all other factors also being common to the four steels. The only variable is the casting temperature. The four steels were cast at temperatures of 1620°, 1580°, 1535° and 1500° C. respectively, and the last one was the only one with an equi-axed structure. Two additional steels in the series showing the same structure as the latter steel were cast at the same temperature. In this particular instance the critical casting temperature with regard to structure is 1500° C.

If the macrostructure has any effect on the mechanical properties it must be so slight as to be readily annulled by the influence of other factors, because steels with columnar structures give exceedingly good results and also very poor results, as do also steels that are structureless.

Micro specimens of all the steels were obtained and examined and photographed in the as-cast, annealed, and normalised and tempered conditions. The microstructures, however, did not give the slightest indication of what to expect in the way of mechancial test results.

All the steels were given two separate heat-treatments, an anneal at 920° C. for 2 hours and a normalising and tempering treatment consisting of normalising at 880° C. for two hours and air-cooling followed by tempering at 640° C. for 2 hours and air-cooling. The actual rate of heating was not observed, but it was identically the same for all the steels, which were heat-treated in the form of the clover-leaf test bar.

The results of the tests after heat-treatment confirmed what was anticipated, viz., a very slight improvement in the yield point and maximum stress over the as-cast results and practically no difference between the annealed and the normalised and tempered steels with regard to these two tests. The impact value, reduction of area and elongation are the properties most affected by heat-treatment, the elongation not being improved to the same extent as the reduction of area or the impact value. The results indicate that the impact properties are improved by heat-treatment to a much greater extent than the reduction of area or elongation, and, also, that a greater improvement in any property is obtained from a normalising and tempering treatment.

Method of Manufacture

Nine of the steels were made by the basic high-frequency process, nine by the basic electric arc, nine by the acid high-frequency, three by the acid electric arc, three by the acid open-hearth and fifteen in the Tropenas converter. Comparing the 18 basic steels with the 30 acid steels, there is practically no difference in the mechanical-test results except with regard to the reduction of area and impact value. The basic steels have a slight superiority only with respect to the impact strength. This applies to all conditions of the steel.

It is apparent from a close study of the test results that, with one or two noticeable exceptions, the Izod figures for the Tropenas steels are more or less consistently low, but even so the above generalisation still holds when the results of the Tropenas steels are excluded from the acid-steel group. Any statement regarding the relative merits of individual processes in the acid group would be at least tentative. The number of heats in two instances is only three and in the other two instances nine and fifteen. As previously mentioned, however, with only one exception, the impact values of the Tropenas steels are consistently low in the as-cast condition and even in the annealed or normalised and tempered conditions are greatly inferior to the acid high-frequency steels.

Industrial Applications of the Rare Earth Metals

By R. C. Vickery, Ph.D., M.Sc.

In view of the growing interest in the subject of the rare earths an attempt is made to present, in a concise form, an indication of the many uses to which rare earth metals have been put either individually, as a group, or in their naturally occurring forms.

DUE to the growing interest evinced by chemists in recent years on the subject of the rare earths, it may be considered inevitable that industrialists should investigate the applications of this group of some fourteen closely allied elements to their particular industries. Impetus to this study, originating perhaps in Welsbach's successful production of an incandescent gas mantle, has been given mainly by the ceramic industries although it must not be assumed that the metal industry has lagged behind in this respect. Metallurgical chemists prefer working whenever possible with pure substances, whereas the ceramists are accustomed to employing crude materials, as many commodities employed in ceramics do not require initial purification or separation. The main difference lies in the difficulty of maintaining a supply of comparatively pure material —the problem of individual separation of the rare earths is rather an intricate one. Other industries have also shown interest in possible applications of the elements from cerium to lutecium ; textiles, medicine, cosmetics and the electrical industries are all represented in the literature[1] and this paper may be regarded as an attempt to present in a concise form, an indication of the manifold uses to which the rare earths have been put either individually, as a group, or in their naturally occurring forms.

The Ceramic Industries

The property held by the rare earth metals of absorption of ultra-violet rays has been extensively exploited in the manufacture of glasses of which this is a necessary characteristic, i.e. welding goggles.

In the main, cerium and the didymium salts are those most frequently employed for this purpose, 2–4% Ce_2O_3 rendering glass completely absorbent of ultra violet rays.[2] The infra-red absorption of glasses containing the rare earths is also of interest, but as yet little progress has been made in the application of such glasses. The irradiation properties of cerium have also been utilised in fluorescent tubes employed with mercury vapour lamps ; before the beginning of the war, there had been an attempt to replace the neon advertising lights either by such fluorescent tubes or by utilising tubes of fluorescent rare earth glasses instead of the normal coloured tubing, but with the commencement of hostilities and "blackout" precautions such novelties were abandoned.

Coloured glasses may also be obtained by use of the rare earths, in fact the only bright purple colour known in glass is that produced by the inclusion of neodymium ; the other elements give colours ranging from grey to green, or in combination with cobalt–red. As well as a colouring effect, the rare earths have been employed for the decolourisation of glasses, mixtures of cerium and neodymium being used, the cerium oxidising the bivalent iron to the tervalent form whilst the reddish colour produced by the neodymium compensates for the green of the ferric iron. Ceric oxide is assuming importance also in the field of glasses employed in X–ray work as it was found that Ce_2O_3 could replace the manganese usually employed as an oxidising agent without the production of the colour which glasses containing the latter element develop on prolonged exposure to X–rays. In connection with the colouring and decolourising properties of Ce_2O_3 it is interesting to note that the dioxide has an opacifying action on enamels, in which 2% of the oxide is equivalent to 5% SnO_2,[3] the process would however seem too expensive to warrant extensive usage. One further use to which neodymium and praseodymium have been put is the production of artificial gem stones—the purple colour produced by these elements being particularly adaptable to the faking of rubies.[4]

The Metal Industries

The author has indicated several applications of the rare earths to metallurgy in a previous paper,[5] but as stated above, the main drawback as far as the metallurgist is concerned is the purity of the materials employed. As cerium is the most prolific and easily extracted of the rare earth metals, most of the data available concern that element although the applications of praseodymium and neodymium are being more widely investigated as supplies increase. The two main alloys of cerium are the poryphoric alloy employed for lighter flints and in tracer shells, and " misch " metal, which latter is a very active " getter " for gases in electronic vacuum tubes. The use of cerium in ferrous metallurgy has produced some interesting results although according to Tamman and Ruhenbeck[6] cerium alloys are hardly applicable to use in moist air owing to the disintegration of the intermetallic compounds. It is assumed that this refers also to non-ferrous alloys. In cast iron, the addition of cerium has a strong deoxidising and degraphitising action which leads to a whitening of the general structure, whilst in steel the depth of hardness is increased to a certain extent. Generally, cerium has also a grain refining action on alloys in which it is included. Several patents[7] have been taken out relating to the inclusion in alloys intended for use as heating elements, of the rare earth metals in quantities up to 2%, whilst up to 6% of the rare earth metals has been introduced into an alloy for the manufacture of surgical needles.

1 Gordon, The Rare Earths and Minor Metals,—a bibliography, John Crerar Library, Chicago 1941.
2 Ctyrosky, *Sklarske Rozhledy* **15**, 23, 1938.
3 Brit. Pat. 488,008.
4 Quasebart. *Umsch. im Wiss. u. Tech.* **38**, 244, 1943.
5 METALLURGIA. June, 1944.
6 Z. Anorg. *Allgem. Chem.* **223**, 288, 1935.
7 U.S. Pats. 2104835, 2174919 ; Brit. Pats. 429492, 510236 ; Fr. Pats. 770112, 785076 ; Ger. Pats. 632657, 722506.

Investigations upon the influence of the rare earth metals upon non-ferrous metals and alloys have been mainly concerned with their effect upon Al, Mg and their alloys, and here again, the rare earth metal most commonly employed in the researches is cerium. Controversy originally arose concerning the exact influence of this metal upon the lighter alloys, but it would appear from a critical study of the evidence available that arguments for and against the use of cerium have been created by the differing properties investigated by the various workers. From the data available however, it is possible to obtain a fair idea of the effect of cerium and although some properties of the alloys deteriorate, the consensus of opinion inclined towards its inclusion for special purposes. Thus although at high temperatures the solubility of hydrogen in aluminium is increased, and in Avional and Aldrey the inclusion of cerium lowers the tensile strength and corrosion resistance, with increase in the electrical conductivity in the higher alloys it prevents the formation of the brittle FeAl constituent and renders the alloy very resistant to corrosion. Casting properties may be less satisfactory, but the resistance to stress and beneficial effect upon the elongation, hardness and microstructure, are factors which cannot be overlooked,[8] whilst corrosion resistance is further enhanced by the production of an abnormally thick anodic oxide coating in chromic acid.[9] In magnesium, cerium apparently increases the ductility and strength whilst Haughton and Schofield state that some alloys are feebly magnetic; the author however considers that such magnetism as may have been observed would be due, not to the inclusion of cerium, but to the presence of adventitious didymium or dysprosium compounds.

The study of the influence of rare earth metals other than cerium has apparently been confined to praseodymium the influence of which upon several non-ferrous metals has been investigated by Canneri[10] who found that in general the compounds and alloys with Pr are all hard and brittle. Rossi and Chini also examined the compounds $PrSn_3$ and $PrPb_3$ and obtained results comparable to those obtained by Canneri.

The Chemical Industries

The importance of the rare earths in industrial catalysis has been pointed out by Hopkins and Taebel,[11] and it would appear that as alloys or oxides they are being employed in increasing amounts for this purpose. From the literature it is seen that, so far, the main applications have been in the organic field, particularly concerning the reactions of aliphatic compounds, although the use of cerium fluoride in carbon pencils for arc lamps to increase the brilliance of the light, may be considered to a certain extent an example of inorganic catalysis.

Biological Applications

Although possibly rather incongruous in this journal, the uses of the rare earths in biological chemistry and its allied sciences may be of interest to some readers, particularly the orticant effect of the metals upon the nervous system when inhaled—this may preclude the employment of the metals to any large extent in welding operations during which the rare earth metals may be vaporised and inhaled by the worker.

It has been found that doses of erbium and cerium salts increase the hæmoglobin and red cell contents of the blood—this anti-anæmic property is apparently greater than that afforded by iron compounds, but as the salts are relatively poisonous and increase the blood coagulation rate, there would appear to be but little future for this method of treatment. Cerium oxalate has occasionally been employed against sea-sickness, whilst the iodide has an inhibitory action on cancerous tissues. In general the rare earth salts have an antiseptic tonic and astringent action on the human body and in plants influence the growth and increase the fruit yield.

In conclusion it may be stated that a great amount of work is necessary before the applications of the rare earth metals can be systematised. Many industries may be affected by their use, such widely variant commodities as pharmaceuticals and textiles being possible fields for exploitation—in the latter industry, the rare earths, together with tin salts are being progressively employed for the purpose of delustring rayon, weighting silk and rayon, mordanting and increasing the lightfastness of dyes. The fields of application are unlimited, and without a doubt many processes involving the rare earths, at present kept secret for security reasons, will be manifested upon cessation of hostilities.

8 Baukloh & Rediall. *Metallwirtschaft*, **21**, 683, 1942. *Khim. Referat. Zhur.* 4, No. 6, 89, 1941.
9 Okamoto. *Jap. Nickel Inf. Bur. Tech. Inf. B.* **18**, 1938.
10 *Met. ital.* **26**, 794,869, 1934.
11 *Tr. Electrochem. Soc.* **71**, 45, 1937.

Electrochemist of the U.S. Bureau of Standards awarded Acheson Medal and $1,000 Prize

THE Board of Directors of The Electrochemical Society announces the award of the eighth Edward Goodrich Acheson Medal and Thousand Dollar Prize to Dr. William Blum, Chief of the Section of Electrochemistry, U.S. Bureau of Standards.

Dr. Blum is to a very large measure responsible for the standardisation of electroplating methods and of plating formulas. He has been with the Bureau since 1909 and for a number of years he was closely associated with Dr. W. F. Hillebrand, former Chief Chemist of the Bureau. The formal presentation of the Gold Medal and $1000 Prize took place at the full convention of The Electrochemical Society at Buffalo, New York, October 13, 1944.

A Metal Cutting Invention

A NEW method of metal cutting which may revolutionise the sheet metal industry and will, in many instances replace the expensive steel-die process, has been invented by a U.S. Army Corporal of Polish descent named Milton Berlin. The method provides a means by which the gap between precision die and hand work can be filled. Its limitation is that it can only be used on metals up to certain thicknesses, but in the production of many war components this new method is invaluable.

Applying this method sheet metal can be cut up $\frac{1}{8}$ in. (3·2 mm.) thick in aluminium and aluminium alloy and up to $\frac{3}{32}$ in. (2·4 mm.) thick in steel with an accuracy of 0·005 of an inch (0·125 mm.). The time required for the procedure can be cut 60 per cent. by this new method which is being kept on the secret list until after the war.

The Coinage Metals in Antiquity

Part I.—Punjab and Egypt

By Douglas Rennie Hudson, B.Sc., Ph.D.

(*Lecturer in Metallurgy, Heriot-Watt College, Edinburgh*).

"*If modern Oriental research has taught us nothing else, it has at least taught us that literary culture is immensely old in the valleys of the Euphrates and the Nile. It has shown that the civilisation and culture of to-day are not the first the world has seen; that in the days of Moses education and literary ability were as fully developed as they were in the days of our immediate forefathers, and that in still earlier days books were read and written, the law was codified, libraries established, the Arts and Sciences studied and known.*"—A. H. SAYCE, 1903.

ABSTRACT.

The historical development of gold, silver, bronze and *electrum* artefacts is reviewed under the headings :—

1. INTRODUCTION.—Bronze and copper, Provenance of the tin in bronze.
2. INDUS BASIN AND BALUCHISTAN.—Metal working.
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The fine workmanship in pre-dynastic Egypt before 3400 B.C. is illustrated. Four peaks of craftsmanship in three millenia can be recognised. Metals and ores are not indigenous and process skill was inferior to that of races less advanced culturally—e.g., Assyrians and Hittites. The following theory is proposed : The earliest bronze found at Ur in Irak was manufactured round Lake Van, where metallurgical skill had always been high. This was not exported to Egypt, which obtained copper from Cyprus, but to Sumer. When Asiatic tin deposits failed, the bronze supply dried up, leading to the use of hammered and modified coppers with low alloying content of arsenic, nickel or antimony, in Sumer ; these are the first *ersatz* metals. Later, bronze—manufactured from Cyprus copper and tin imported by Phœnicians from Spain or Cornwall, was introduced into Egypt and Irak, giving a second bronze age in the latter. The Iranian plateau which saw the beginnings of process metallurgy, is proposed as the cradle of the *Wiro* Aryans.

1. INTRODUCTION

PERIODS now regarded as impossibly early were assigned in the nineteenth century to the first dynasties in Irak and Egypt. These two areas show remarkable analogies, in cultural levels, artistic attainment, continuous internal warfare, and even in the means whereby their ancient chronologies have been restored. But most striking of all is the similarity in their political systems. Egypt was composed of semi-independent *nomes* (*chsap*, Gr. νομος) each ruled by a noble *chika*, often high priest to the purely *local* deity. In Mesopotamia the constitution was similar, the *patesi* or chief priest acting as mouthpiece to the *local* god. An enterprising *patesi* lost no opportunity to become a kinglet (*lugal*) by increasing his domains. There resulted a mosaic, of city states like early Babylon, semi-independent towns like Lagash and Tello, countries like Akkad and Sumer ; the overlordship of this pattern changed periodically. Thus both countries were *quasi*-federal in structure, to this one can attribute their success in maintaining such an advanced civilisation despite wasteful internecine conflict, just as the cohesion of Germany after 1918 is attributable to the large number of cities and states with reserved rights, and the efficiency of local administration in these. Politically, these two old countries are quite comparable with the pre-1914 multi-coloured tartan of the German Empire.

In both countries the rivers rose annually with the melting of snow at the head waters. Egypt owed its fertility, indeed its very existence as a cultivated strip in the desert, to the burden of rich alluvium deposited from the floods ; failure or deficiency was a catastrophe of the first magnitude. In Mesopotamia the flood was never anything but a nuisance.

Recent excavation in Anatolia, Macedonia, and the Persian massif have yielded highly interesting results. Investigation of the numerous *tells* (natural mounds heightened by accumulation of refuse from inhabited houses) in Palestine has been uniformly disappointing. "The modern peasants live in houses practically identical in style and construction with those which sheltered the peasants of 2000 B.C.—a community of white ants could not be more unprogressive."—MACALISTER.

Yet, in hackneyed phrase, the remarkable remains of the Indus basin and Baluchistan have been "scarcely scratched," and investigation under the ægis of the government of India has been carried out most carefully and systematically.

Bronze and Copper.—For long the archæologists regarded an area between the Caspian and Aral seas

as the cradle of civilisation. From here divergent streams issued, congealing into three foci—Egypt, Irak, and the Punjab, with cognate Baluchi culture. Later excavation in Asia and Siberia may yield other foci of which we are as yet ignorant. In the valleys of the Nile, Euphrates and Tigris, metal working had reached an extraordinarily high level between five and six thousand years ago—yet in neither country was native metal or ore indigenous. From consideration of the copper-bronze-copper sequence the author will attempt to show a "bronze age" preceding the "copper age." As Macaulay's schoolboy would know, bronze is more easily castable than copper and has a lower melting point, but for some reason it went out of use and was replaced by copper. Many artefacts of copper are hardened by cold-hammering to an edge, some contain small and varying contents of alloy, like arsenic, nickel and tin; these we may term "modified" coppers (the word *not* being used in the technical metallographic sense associated with aluminium alloys). These are the first examples of *Ersatz* alloys.

Provenance of the Tin in Bronze.—As yet, no safe conclusion can be drawn regarding the origin of the tin. Lay opinion has always inclined to Cornish ores, said, on rather inconclusive evidence, to have been exploited by the Phœnicians. These, like Strabo's Persian deposits, are a possible source, but the assignment is by no means certain. The whole question is bound up with the reason for the sudden failure of the bronze supply, which the author would attribute to exhaustion of tin. This would rule out the Cornish field which is still producing. He attributes the whole bronze of Sumer, Susa, Iran, Punjab, to an external provenance—Cappadocia or near Lake Van (i.e., near the Mount Ararat of the Old Testament, where Noah's ark was said to have settled). Whether we can credit this manufacture of a true bronze of fairly constant tin content at 10–12% to the Hittites (or Mitanni, their predecessors) or to Urartu near Mount Ararat, only further excavation will show. In process work all these peoples show a metallurgical competence high enough to justify the assumption. But in the case of the three foci—Egypt, Irak, Punjab—there is evidence of little if any skill in ore extraction, and we conclude that they imported bronze as a working material.

In a previous paper the chelate area enclosing the incunabula of metal working in the near east has already been indicated; it corresponds approximately to Breasted's fertile crescent, including the basins of the Nile, Euphrates and Tigris, Anatolia and some Mediterranean islands, particularly Crete and Cyprus. This is *not* coincident with the region, including the incunabula of metal extraction, which is shown to lie rather northwards, but the areas overlap.

Origin of the Wiro Aryans.—The origin of the great primitive people which invented, developed and spread the Aryan language, adopted by so many races—northern *Nordics*, *Alpines* of Central Europe, and *Mediterranean* peoples in the south—has caused great controversy. (In discussion, more than usual circumspection is necessary, philological corns being very tender.) This remarkable people has been called *Wiro*, a name synthetised from Aryan words meaning "men." Greatly daring to tread on philological ground, the author will suggest that their origin is not in the interval between the Caspian and Aral seas, nor in Sumer, but in the Asian *massif* where process metallurgy (not metal working) had its origin.

2. INDUS BASIN AND BALUCHISTAN

Although the Indus civilisation was spread over a far greater area than either the Egyptian or the Mesopotamian, a remarkably homogeneous level was attained. The script has not yet been deciphered, it is much more primitive and rough in execution than the hieroglyphs of the Nile or the wedge script of Sumer, and shows no similarity to either. Taylor has discovered an analogy with the curious inscriptions of the wooden tablets of the lonely Easter Island in the Pacific, which are not likely to be more than three centuries old and may be much less.

Metal Working.—The artefacts include tools, bowls, weapons and jewellery, especially the characteristic disk beads (Fig. 1). Bronze of varying composition, coppers modified with nickel and arsenic and copper alloys containing as much as 4½% arsenic, gold, silver and electrum have been found. Hammering, casting by *cire perdu*, riveting and making secure by "running on" molten metal, were efficiently carried out. Apparently soldering and sweating were not very familiar; this is in marked contrast from the intricate filigree and granular goldsmithing of Ur, with which the Indus culture has been compared, not altogether happily. Micro-examination of the bronze objects has shown that many were *hammered after casting*. Plenderleith has deduced that the early Punjabi metallurgists were familiar with the plastic range of bronze, and were accustomed to forge it "just below redness." If this be valid, it would indicate a high workshop competence.

Dating of the finds is much less certain than in Irak or Egypt, a doubt which the pre-historian will clear up as more information becomes available. The bronze has been attributed to pre-3000 B.C.—i.e., approximately contemporaneous with that of Sumer, which preceded that of the Old Kingdom of Egypt by about five centuries. This alloy was not plentiful or in common use, perhaps owing to rarity of tin.

3. NILE VALLEY

Chronology

The chronology of Egypt is remarkably well authenticated over a period of over 6,000 years, and such discrepancies as remain are being dissipated almost with every new digging.

Manetho's record, written in Greek about the third century B.C., and at one time implicity accepted, is now regarded as semi-mythological, but his dynasties form such a convenient framework that they have been preserved by nearly all Egyptologists. No credence is attached to his explicit dates, and many of his kings are mere *nome* princelings.

More correct dating is available by dead-reckoning, by data from the Palermo stone, the Royal Canon of the Turin papyrus, and tomb inscriptions from Abydos. Yet the best results are obtained by interpolation of all these into astronomically fixed points, a method so successfully applied by MEYER.

"In the Delta civilisation probably advanced and the calendar year of 365 days was introduced in 4241 B.C., the earliest fixed date in the history of the world as known to us. A long development, as the 'Two Lands' which left their imprint forever after, on the civilisation of later centuries, preceded a united Egypt, which emerged upon an historic horizon at the consolidation of the two kingdoms into one nation under Menes about 3400 B.C. His accession marks the beginning of the dynasties, and the preceding, earliest period may be

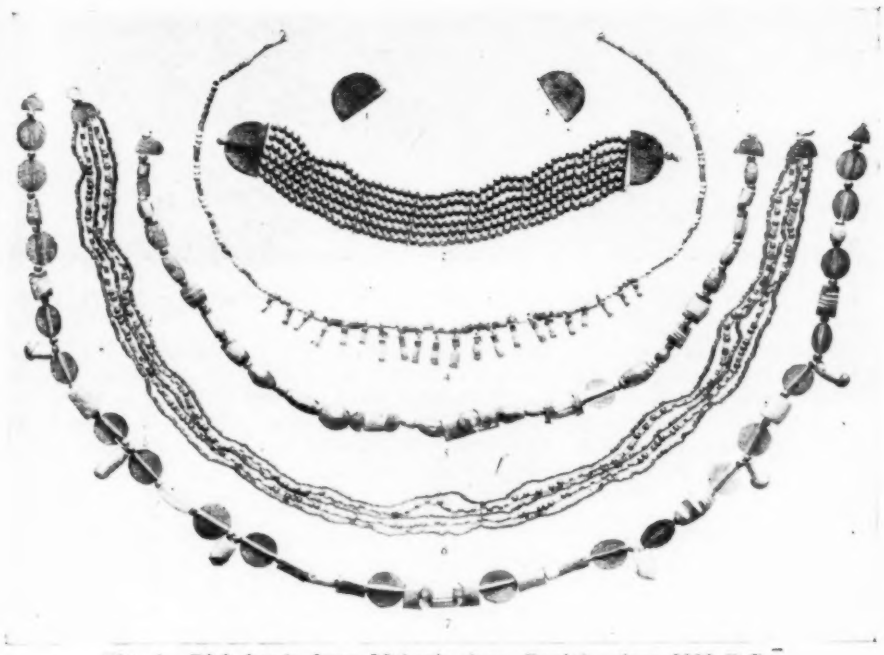


Fig. 1.—Disk beads from Mohenjo-daro, Punjab—circa 3000 B.C.

conveniently designated as the pre-dynastic age."—BREASTED.

Early Calendar Fixing.—Delta civilisation was the more advanced, we know little of it, buried under about 30 ft. of Nile alluvium. Early computers devised twelve months of thirty days with five feast days at the end of the year—a system of interest to present-day calendar reformers. This is much simpler than the less consistent and cumbersome Julian system, imported to Rome from Egypt by the enterprising Cæsar and now in use everywhere in the Gregorian calendar.

Pre-dynastic Delta Astronomy.—The day when Sothis (*Sirius*) rose on the horizon at dawn was taken as the beginning of the official year; presumably on an average the Nile floods reached the lower Delta at that date enabling the spring sowing to be begun.

A calendar with 365 days would gain a whole day in four years or a whole year in 1,460 or 1,461 years! This *Sothic* cycle leads to the most important conclusion that the calendar was introduced on 19 July 4241 B.C.(Julian). Early attempts to correlate the incommensurable solar year of 365·2422 days and the lunar month, led to frequent juggling with the almanac. In the havoc which this played with the chronology the 1461 year precession gives a first-rate set of astronomical pegs, the eclipses being religiously observed and recorded. An alternative date for introduction of the calendar is 4236 B.C. Thus astronomy flourished a millenium before Menes.

A people able to perform the complex computations necessary to establish a calendar *ab initio* is in no mean state of intellectual attainment. Had we any of their metal objects these might be found to rival Petrie's glorious pre-dynastic relics.

Scripts

Three characters were used on the Nile :—

(*a*) *Hieroglyphs.*—The pictograph, depicting the object portrayed, was gradually idealised into the hieroglyph, but the engraving on stone was carefully done, and the outline was close enough for easy recognition. This script was used from pre-dynastic centuries—some archaic hieroglyphs have not yet been elucidated—for monumental work. It was used for writing on papyrus from about the second dynasty, say, 3200 B.C. None of the early writings has come down to us, but it is clear on several counts that the character was then very old—to cite only one : The involved astronomical computations would necessitate some script and numeral notation. One may contrast the brilliant Greek mathematical intellectualism with the poverty of the Romans hampered by their clumsy notation.

In their trading outpost at Byblos in the Levant, the ancient Egyptians taught this picture writing to the native Giblites, who preserved it without having the enterprise to modify it in the slightest. Consequently it persisted unchanged here—like Elizabethan words of New England now current in the language spoken in U.S.A., and the Tudor ballads of remote Appalachian villages—for about a millenium, long after it has been discarded for use except in monumental engraving, in the land of its origin.

(*b*) *Hieratic.*—"The attempt to write these figures rapidly with ink upon papyrus had gradually resulted in reducing each sign to a mere outline, much rounded off and abbreviated. This cursive business hand, which we call *hieratic* had already begun under the earliest dynasties, and by the rise of the Old Kingdom [2980 B.C.] it had developed into a graceful and rapid system of writing, which showed no nearer resemblance to the hieroglyphic than does our own handwriting to our print.

This useful script persisted to the end of the Ethiopian dynasty and for religious purposes as late as 200 A.D.

(*c*) *Demotic.*—This script was derived from the speech in current use, better suited to business and administration. For religious inscriptions, however, the hieroglyphs still retained a ceremonial value, like sham-Gothic lettering in this century.

Thus the three hands are not distinct, but have evolved in succession. Clement of Alexandria mentioned them, and Pythagoras learned them during his stay in Egypt. Herodotus mentioned the *cursive* and *demotic* scripts, but not the *hieroglyphs*. Signs for plants of swampy habitat not found in Upper Egypt point to Delta origin of the latter.

The *demotic* script was elucidated from an engraved basalt slab called the Rosetta stone, from the place of

its recovery by one of Napoleon's officers during his invasion of Egypt. It was one of the *stelae* set up by Ptolemy V (Epiphanes) in laudation at his coronation. In the interest of indirect rule, the Roman power included *hieroglyphs* and *demotic* characters in addition to the court Greek. To this care we owe the decipherment of the *demotic*. Comparison of the names Ptolemais and Kleopatra was the first step in explaining *hieroglyphics*. The scholarly Champollion made great the progress, using his knowledge of Coptic—the "modern" Egyptian, which, like Old Slavonic, is extinct as a spoken tongue, but survives in church services and a large sacred literature.

Fig. 2.—Frieze of geese from an Old Kingdom Tomb at Medum (Cairo

The Alphabet

Phœnician Adaptation.—Papyrus gradually spread to the Phœnicians; no people could be better suited to diffuse a convenient accounting device than these enterprising traders. The cursive (*hieratic*) hand rapidly displaced their wedge characters, an anachronism from Sumer. By the tenth century B.C. they had developed it into a system of *consonants* which rapidly travelled to the Ionian Greeks, and thence to the Roman and Russian alphabets, which have served so great a part of the world's commerce and literature.

Analysis into Letters.—Even before King Menes, the scribe used "not only phonetic signs representing a whole syllable or group of consonants (i.e., as in modern Japanese), but also the *alphabetic* signs, each of which stood for one consonant; true alphabetic *letters* having been discovered in Egypt two thousand five hundred years before their use by any other people. Had the Egyptian been less a creature of habit, he might have discarded his syllabic signs 3,500 years before Christ, and have written with an alphabet of twenty-four letters."—BREASTED.

Early Metal Working in Egypt

Early Dynasties.—The fine design and consummate craftsmanship of pre- and proto-dynastic work is now generally appreciated, and not only in metal-working. See, for example, the *élan* and the confidence in the draftsman's pencil in the geese frieze (Fig. 2), the fine modelling in the bas-relief of Prince Hesire in wood (Fig. 3), the strength and dignity of the lion's head in hardest granite from the Sun-Temple of Nuserre (Fig. 4). Numerous other objects, equally fine, have been preserved from the Old Kingdom.

The first and second dynasty period, 3400–2980 B.C., represented four centuries of great prosperity. Trade was vigorous with Crete, Cyprus, Aegean islands, Asia Minor, Persia and Irak, the arts flourished, administration was efficient and Egyptian dominion was extended

Fig. 3.—Bas relief of Prince Hesire in wood—Old Kingdom.

Fig. 4.—Lion's head in black granite from the Temple to the Sun of Nuserre—circa 2850 B.C.

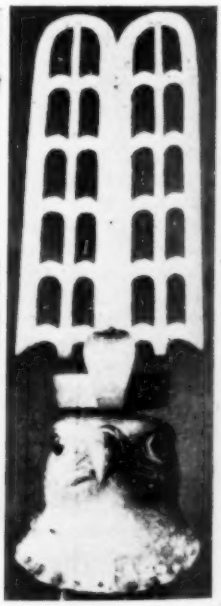


Fig. 5.—Head of sacred hawk in gold.*

*The head shown in Fig. 5 was found associated with the well known statues of King Pepi I and his son Montesuphis of the IVth dynasty. The eyes, polished ends of an obsidian rod, give an astonishing insolent expression. The head is crowned by a plume of conventional feathers. Circa 2400 B.C. (Cairo Museum).

(Cairo Museum). **In the original the two sections formed balanced halves of a panel.**

southwards *vi et armis*. Menes, formerly a mystical deified figure, has emerged from the mist of antiquity as an historical monarch, probably a compost of three individuals. He unified the (red) Delta with (white) Upper Egypt, hence the double crown and the colours of the united kingdom. The capital was at the obscure Thinis, near Abydos, where Petrie discovered so many fine metal and other relics in the Royal Tombs.

Shemsu-Hor, the Blacksmiths (?).—Pre-dynastic kings from the western delta, or perhaps Lybia, Shemsu-Hor, the Falcon Clan or followers of Horus, who penetrated the country in the fifth millenium B.C., are sometimes regarded as smiths and metal workers. The god is said to have been established in a shrine at Edfu with a forge behind the sanctuary. It has been claimed that smithy work was a priestly privilege and that *iron* was actually worked. There is no evidence to support this, and the whole interpretation is highly speculative. Manetho referred to them merely as "the dead" by this time they had become deified.

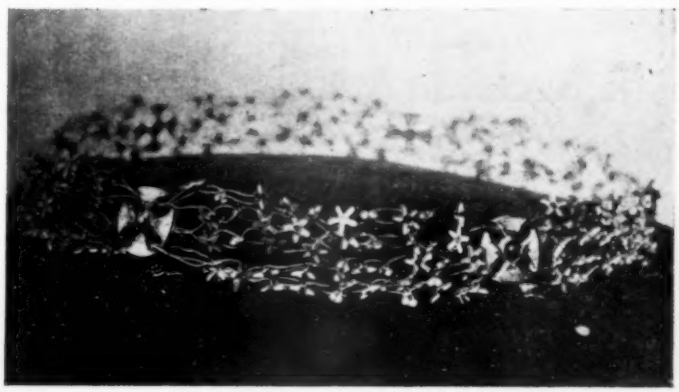
Peaks in Metal Craftsmanship

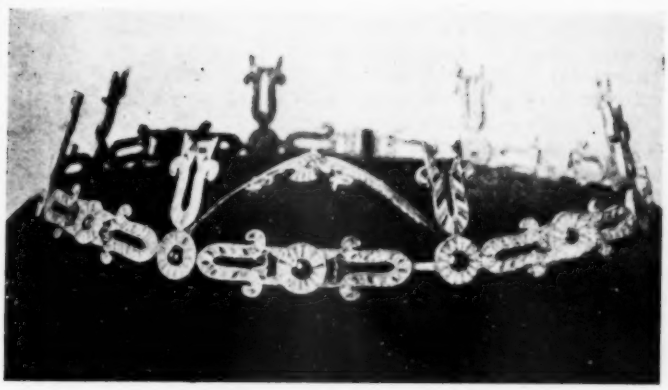
Pre- and Proto-Dynastic.—Reisner recovered some magnificent first dynasty gold ornaments from a cemetery at Naga el Der. The capsule has the Neit sign inlaid. So fine is the fashioning of the bull and gazelle that they would pass to-day with the layman (or woman) as high-grade hand-beaten gold work, such as was produced in Vienna immediately before the present war. The quality of the craftsmanship is far higher than that in the greater part of such work produced in this century, and compared with it Victorian work is barbaric.

Such masterpieces are of no mushroom growth, requiring an acme of technical skill and generations of artistic tradition to come to fruition. In Ancient Egypt this was especially applicable, respect for established design being carried to fantastic length (*and I say ten thousand years not as an expression but as a fact.*—Plato.) It is clear that jewel-making was a highly developed craft centuries before King Menes. In the Old Kingdom the statue of Pepi I and his son in copper shows remarkable vigour.

Fig. 6.—Jewelled bracelets recovered from Abydos. 1st dynasty 3400—3200 B.C. (Petrie: Royal Tombs).

The gold bracelets are set with lapis lazuli, amethyst, turquoise, and show excellent workmanship.





Figs. 7 and 8 show diadems of the XIIth dynasty princess from Dashur.

The gold work is set with red jasper, carnelian, and lapis lazuli or green felspar.

Many important discoveries of early metal objects are due to PETRIE. Fig. 6 shows four really magnificent bracelets from the skeleton arm of a first dynasty princess, *circa* 3400–3200. We owe the preservation of these priceless relics to a peculiar circumstance. The early burial at Abydos was rifled of its gold and gems after a thousand years. Presumably disturbed in the act, one of the robbers stuffed into a convenient hole in the wall "the desiccated arm of Zer's queen, still bearing under the close wrappings its splendid regalia. Perhaps slain in some brawl, the robber fortunately for us, never returned to recover his plunder, and it was found there and brought to Petrie intact by his well-trained workmen in 1912."

Middle Kingdom.—Figs. 7 and 8 show diadems of a princess of the twelfth dynasty (2000–1788) in Cairo Museum. The first is simply a golden band with stylised flowers of red jaspar, carnelian, lapis lazuli or green felspar, with a rosette of gold between each pair. From other rosettes conventional flowers rise vertically. In the second, "a light network of golden wires carries on its threads little florets and berries of coloured stone. At six points the threads are gathered up and fastened to Maltese crosses" inlaid with blue, with a carnelian stud at the centre. Who will dispute Petrie's judgment? —*The floret crown is perhaps the most charmingly graceful head-dress ever seen.* BAIKIE has expressed the position admirably: "The Dashur jewellery puts to shame most of what passes for good work in the same kind at the present day." In working and design these coronets vie with the finest productions of the Italian master Cellini.

The Empire.—During the six centuries of this period a remarkably successful imperialism was slowly and consistently pursued. Great expansion of the domains owing allegiance to the crown was secured. The enormous tribute which flowed into the treasury at this time led to a vigorous internal prosperity which was reflected in the fine craftsmanship.

For example, the chief treasurer on one occasion brought in "chariots of silver and gold, statues of ivory and ebony, necklaces of every costly stone, weapons of warfare, and work of all craftsmen."

The Saite Restoration.—Under the twenty-sixth dynasty a great attempt was made to restore the old glory, with apparent success. Greek influence was eagerly accepted and permeated the country, but the renascence was too late and too superficial to save the country from conquest by the Persians under Cambyses in 525. From this the country never recovered.

During the Restoration some magnificent cast-bronze figures were produced, elaborately inlaid with gold, silver and electrum. Large hollow statues were common, and most of the Egyptian bronzes in the museums of the world belong to this period. Great interest was taken in anatomy, and the *demotic* script was introduced.

Thus we may trace several peaks of artistic attainment, not only in metal craftsmanship but in engraving, sculpture, and architecture—

PRE-DYNASTIC	before 3400 B.C.
MIDDLE KINGDOM (especially XII dynasty)	2160–1788 B.C.
THE EMPIRE (especially XVIII dynasty)	1580–1090 B.C.
SAITE RESTORATION (XXVI dynasty)	633– 525 B.C.

Between these were intervals of decadence, usually called the "Dark Ages." The best known is the period of Hyksos or usurpers, who ruled for about two centuries, between Middle Kingdom and Empire. Penetrating from the north-east, they introduced the horsed chariot, new computation methods, bronze weapons, and perhaps rudimentary alphabetic signs. Thus they possessed a high cultural development, nevertheless the country fell into a state of degradation under their rule. Khurri, Hittite, Mitanni and Cretan origins have been suggested for them.

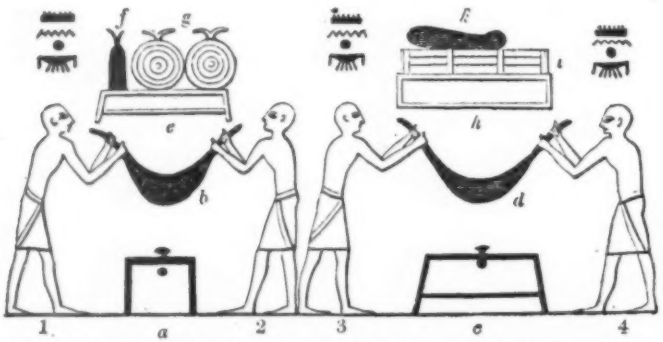


Fig. 9a.—The hieroglyph on this rock carving at Thebes is rendered "mench nub" and construed "worker in gold." It is tempting to explain the operation as the squeezing of surplus mercury from solid amalgam, but the process was probably not then known. More probably the artificers are working bellows.

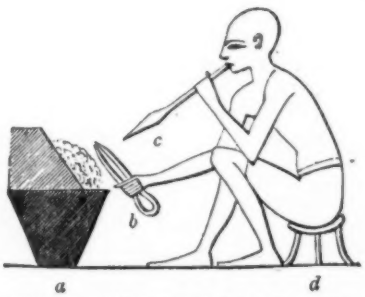


Fig. 9b.—Rock carving from Beni-Hassan showing a naked craftsman urging a primitive forge with the mouth blowpipe.
After Wilkinson.

Status of the Metallurgist

Leaders of Expeditions.—There is no doubt that, in the Old Kingdom, metalliferous mining was a "learned profession" with monarchs like Seti I and Rameses III (1198–1167 B.C.) taking charge of prospecting expeditions or at least claiming the credit on engraved *stelae*. Some of the Sumerian gods were metallurgists, the blacksmith-priests of the Falcon Clan (of doubtful authenticity) have been mentioned. On the other hand, the artisan was ill-paid and sunk in degradation, merely a skilled serf; the material status of the craftsman producing fine jewels was little higher. *I have never seen a smith on an embassy nor a smelter sent on a mission—but I have seen the metal worker at his toil at the mouth of his furnace or forge, his fingers rugged as the crocodile.*—SALLIER PAPYRUS. What metallurgist to-day, be he process man, metallographer or assayer, be he apprentice or director, in whom this old indictment, written so many centuries ago, does not arouse a touch of fellow-feeling?

Dues and Wages.—Besides poll tax and rates, the individual worker was liable to tithe in kind, whether

craftsman or peasant. As a result the temples developed grandiose stores filled with merchandise—grain, textiles metals—and gradually set up workshops in which these were fabricated for ceremonial use or for sale. It has even been suggested that the customs house at Baghdad to-day closely resembles a temple store in Irak five thousand years ago, in the bustle, variety, and noise of its transactions. The Egyptian temple came to resemble a mammoth mediæval monastery. An artificer was paid 5 *outen* of copper (bronze ?) *per mensem*, in comparison a bronze razor cost 10 *outen* and a tanned hide 2 (1 *outen* = *circa* 96 g.). In Chammurabi's reign in Babylon a skilled craftsman, responsible for directing unskilled labour, received about 6 *shekels* of silver *per annum* (1 *shekel* = 8·4 g.).

and well authenticated remains of the early workings. According to the Arab geographer Edrisi, or Al Idrisi, these or neighbouring mines were in production using the amalgamation process in the twelfth century A.D. Rock carvings in Upper Egypt (Fig. 10, after Wilkinson) showing washing, weighing, and melting of alluvial gold in the blowpipe, probably apply to these deposits. Under the cruelly abused slave labour described by Agatharchides (in a fragment preserved in Diodorus Siculus) they produced large outputs for centuries. Subsequently some amelioration of working conditions occurred ; each miner was provided with quarters, rations, water and a change of garment every month.

Silver is not found in Egypt. In the early pre-dynastic days it was said to be more valuable than gold, as in

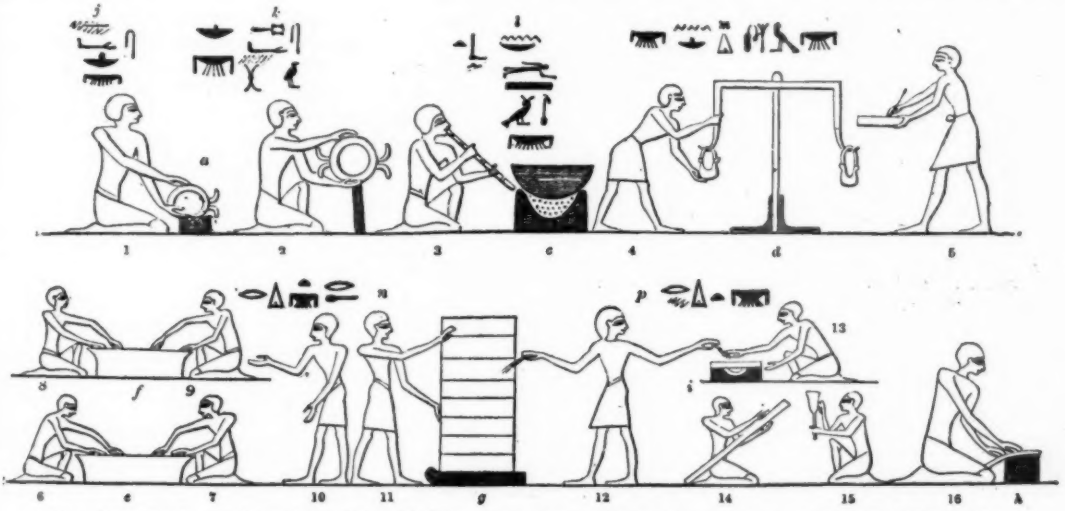


Fig. 10.—Rock carvings from Beni-Hassan show the washing of auriferous material, followed by melting in the blowpipe, and production of jewellery.

The hieroglyphs read :—*j* : works the gold ; *k* : works a gold collar ; *l* : melts the gold ; *m* : gives the gold register of the gold ; *n* : gives gold ; *p* : gives gold.

The operations are in reverse sequence to our own, starting from the bottom right hand. They follow closely Agatharchides' description. The hieroglyph for gold is seen to be a stylized collar.

1 and 2, jewel manufacture ; 3, melting the gold under mouth blast ; 4 and 5, weighing and recording ; 6, 7, 8, 9, pan washing ; 10, superintendent ; 11 and 12, screening ; 13, sieving (?) ; 14 and 15, pounding and washing on inclined tables ; 16, sorting the rough ore. *After Wilkinson*

Craftsmanship.—Despite miserable conditions, workmanship was first-rate. Sweating, soldering, inlay, bronze gilding, and casting by the waste wax process, were carried out with the utmost skill. Chains and collars were an important production, frequently bestowed by the king as insignia and in recognition of faithful service. Rock carvings show gold-beating between skins, in the modern method, the stone hammer and anvil were also used ; by the fifth dynasty (about 2750 B.C.) the very creditable attenuation of 0·001 mm. had already been attained. Carvings, panels, stucco, mummy linen, glass, and even the embalmed body, were gilded by tooling gold foil. Later, fire gilding was used with sal-ammoniac flux ; long before the Roman period, amalgam gilding had been introduced.

Individual Metals

Gold and Silver.—Egyptian gold was obtained chiefly from Punt, now generally identified with Nubia, between Nile and Red Sea. The hieroglyph is rendered Nub, but we cannot say which is derivative. In the Turin papyrus dating from Seti I (*circa* 1230 B.C.) there is even a chart of these deposits and near Wadi Allagi there are distinct

Ethiopia at a much later date. Under Menes silver was two-fifths as valuable as gold by legal enactment (2½ : 1), under the Hyksos twice as valuable, and in the Empire rather more than half (5 : 3). Later the ratio rose consistently, to reach 12 : 1 under the Ptolemys. It was imported from Cicilia in Anatolia, and by 1000 B.C. the rich Iberian deposits were being exploited actively by the Phœnicians.

Copper and Bronze.—Relatively scarce before King Menes, copper, used for ornaments, was nevertheless more plentiful than silver or gold. With gradual development of Sinai mines, it was used for nails, bolts, fastenings for wood and stone in building. Bronze, introduced about the third dynasty (say, 2950 B.C.) displaced it only partially and gradually. It is remarkable that it was introduced into Egypt about half a millenium later than in Sumer. Egyptian bronze is much more variable in composition, intentional synthesis is correspondingly more difficult to support, although the great Roberts-Austen held a contrary opinion. Low and erratic tin contents would uphold the assumption of addition of tin ore to a copper-smelting charge, by accident or intent. But accidental addition is unlikely *per se*, transparent

or more usually *black* tinstone looks very different from bright *green* malachite, the usual ore of those days, and does not much resemble glance or pyrites with their *metallic lustres*. That bronze can be produced in this way was shown by Gowland in actual smelting experiments in a primitive furnace.

The summit of Nile accomplishment was magnificent metal-working rather than any great skill in extraction. In process work they were less skilled than other peoples of lower cultural standing—e.g., Hittites, Assyrians, and the Mitanni, whose kingdom flourished in the fifteenth century B.C. midway between these empires. In comparisons one must hold due regard to date. Even with allowance for outward diffusion it is unfair to compare pre-dynastic Egyptian attainment with neighbouring cultures 1½–2 millenia later. In this connection the absence (or at least great rarity) of iron in Ancient Egypt, notwithstanding the favourable dry climate, is noteworthy.

Comparison with Irak.—As stated, bronze was known in Sumer at least five centuries before it was used in Egypt, although the standard of metal-*working* was certainly not inferior on the Nile. Copper tools, moreover, were used, though not in quantity, by the Badari culture which the archæologists agree in placing at a very early date (Petrie's Sequence 30), perhaps 5000 B.C. Thus, on evidence at present available, copper seems to have preceded bronze in Egypt even if it did not do so in Ur and Anatolia. Here is a pertinent query from metallurgist to excavator ! When it is possible to resume digging after the war, particular attention might be paid to this sequence in Anatolia, Macedonia and Turkestan. Probably it is now too late to expect much evidence from future finds in Egypt, but in view of the confusion of copper and bronze specimens which has occurred in the past, as a result of lay identification from patina without chemical analysis, careful re-examination of museum specimens with the assistance of micro-analysis would be very desirable.

Provenance of the Alloyed Tin.—The origin of the tin ore has long puzzled investigators. Strabo gives two interesting accounts—*The Drangae* (Δράγγαι) [perhaps south-east of the Caspian], *who otherwise are imitators of the Persians in their mode of life, have only sparse supplies of wine, but they have tin* (κασσίτερος) *in their country. . . . 15*, II, 10.

He says that *tin, however, is not found there* (*Spain*) *on the surface of the earth, as the historians blether, but is dug out. It is produced both amongst the barbarians dwelling beyond the Lusitanians and in the tin islands, and it is carried to Massilia* (Marseilles) *from the Britons too. But amongst the Artabrians who live farthest away to the north of Lusitania* (Portugal) *towards the setting sun, he says the ground flowers with silver, tin, white gold* (*since it is alloyed with silver*). . . . *3*, II, 9.

The tin islands are ten in number and lie near together in the high seas, north of the port of the Artabrians. . . . As they have mines of tin and lead (μολύβδου) *they barter these metals and hides from their cattle for pottery, salt and copper* (bronze ?) *utensils* (χαλκώματα) *from the sea-faring traders. Formerly only the Phœnicians carried on this trade from Gades* (Cadiz), *for they kept the sea route secret from others. 3*, V, 11.

But it is hardly conceivable that even the ancestors of the very enterprising Phœnicians can have exploited Portugal or Cornwall by the fourth millenium B.C., the date of Sumerian bronze. Therefore the tin in this alloy probably did not derive from western Europe. The author feels that some explanation on the following lines would fit the known facts : The early bronze of Ur was manufactured by Lake Van peoples, Urartu, pre-Hittites, or pre-Mitanni, for export, raw and fabricated, from their own copper ores and perhaps Persian tin. The nearness of Ur and remoteness of Egypt would explain its absence from the latter since the levels of metal-*working* were approximately equal in both regions. *Neither in Irak nor Egypt was process metallurgy highly developed.* With the exhaustion of tin deposits, the supply of bronze to the Sumerians dried up and they were forced to turn to the *Ersatz* modified copper. By this time Cyprian copper had reached Egypt and eventually bronze was manufactured from this and tin from the west (Lusitania and later the Cassiterides) imported by the Phœnicians. Where the place of manufacture was situated we cannot know—possibly in Cyprus itself. Its location is not very important, since trade was brisk in the eastern Mediterranean even at 3000 B.C., and Cyprus became an important *entrepôt*. The bronze penetrated to Irak to yield the second bronze age, about the same time as it did to Egypt. By this time Sumer had declined and Agade was ascendant, to be displaced later by Babylon.

Aluminium Alloy Aeroplane Landing Mats

Emergency mats for aircraft landing have been used for some time in theatres of operation where normal transportation facilities were available. Steel mats were developed for this purpose. In areas where the mats had to be transported by air, however, the need for a lighter weight mat, with comparable strength to that of the steel mat, became apparent. Aluminium mats, therefore, have been developed primarily for transportation by air.

The aluminium landing mats are similar in design to the steel pierced plank type. The mats are approximately 10 ft. in length by 15 ft. in width. The strength of the aluminium mats is comparable to that of the steel mats, yet the weight per panel is 31·8 lb. as compared to 63·9 lb. for the steel panel.

The mats are formed from aluminium sheets $\frac{3}{16}$ in. in thickness. Two $\frac{3}{4}$ in. parallel ribs are formed in the long section of the panel to add rigidity. Three rows of $2\frac{1}{16}$ in. holes are punched on 4 in. centres with their flanges tubelated to add additional strength and to reduce the weight of the mat. The individual panels are connected by interlocking bayonets and perforations along the edges of the plank.

The mat is bundled for shipment in six sub-bundles of five planks each, forming a master bundle of twenty-nine ten-foot planks and two five-foot planks. The master bundle, together with the clips, weighs approximately 1,000 lb., as compared with 2,000 lb. for the steel mats. The speed of laying a runway from aluminium mats is approximately 250 sq. ft. per man hour as compared to 150 sq. ft. per man hour for the steel mat.

The weight of a runway 150 × 5,000 feet for the aluminium mat is 975 tons as compared to 1,928 tons for the steel. This comparison, translated in terms of cargo airplanes required to transport a runway, as has been necessary in Africa, the South Pacific, China, etc., are 163 airplane loads for the aluminium mats and 322 airplane loads for the steel mats.

Wetting Agents—Their Use in Electro-Plating and Allied Processes

By H. Silman, B.Sc., F.R.I.C., A.I.M.Chem.E.

The use of wetting agents has greatly increased in recent years and further advances are likely in the future as the properties and limitations of these materials become more fully known. Considerable useful information in this field is contained in a recent paper presented by the author to the Midland Centre of the Electrodepositors' Technical Society from which this article is abstracted.*

SURFACE active materials, or wetting agents as they have been more popularly termed, have in recent years found increasing application in electroplating and allied processes. Sometimes the results have been disappointing, due to a lack of appreciation of the properties and limitations of these materials, but their possibilities are so great that their use is bound to increase in this field.

Broadly speaking, the surface active materials have molecules consisting of a long-chain hydrocarbon portion to which is attached a water-attracting, or polar group. There are a large number of atomic groups which function in this way, the most important being the carboxylate, sulphonate and sulphate radicals and their sodium salts. In roughly decreasing order of effectiveness the chief polar groups are the following[1].

(1) $O.SO_2.ONa$, Sulphate group (sodium salts).
(2) $-CO.ONa$. Sodium carboxylate group.
(3) $-SO_2.ONa$. Sulphonate group (sodium salt).
(4) $O.SO_2.OH$. Sulphate group.
(5) $-SO_2.OH$. Sulphonate group.

To these may be added the hydroxyl, nitro, amino nitrate, halide and keto groups, and many others, all, of which can have polar properties, as can also unsaturated bonds when present in the hydrocarbon molecule.

For maximum effectiveness a proper balance must exist between the hydrocarbon chain portion of the molecule and the polar group, since if the latter predominates excessively the material will lack surface active properties, whilst if the former is unduly long the compound will not be sufficiently water-soluble to be of value. If the solubility is too high, however, the molecules will be unable to orientate themselves at the interfaces. The rinsing properties will also be influenced by the solubility since it is obvious that the more highly active a wetting agent is the more strongly it will be adsorbed at the surface. It will then be correspondingly more difficult to rinse away. Such residual films can cause difficulties in subsequent finishing operations.

Soaps

The sodium and potassium salts of the long-chain fatty acids (C_8 and higher) all have surface active properties and this group of substances constitutes the soaps. These are undoubtedly the oldest and most important of the surface-active compounds. Amongst the commonest soaps are the sodium salt of oleic acid (C_{17} H_{33}. COONa), palmitic acid ($C_{15}H_{31}$,COOH) and stearic acid (C_{17} H_{35}.COONa) due to the predominance in nature of the fats from which these soaps can be readily made. The solubility of soaps in cold water decreases as the length of the hydrocarbon chain increases. Thus, sodium stearate having a C_{18} carbon chain is practically insoluble in cold water. The solubility of soaps increases rapidly as the temperature is raised, however, so that an adequate concentration can be obtained for their excellent detergent properties to manifest themselves under practical conditions of usage.

In the compounding of cleaners to promote the peptisation and emulsification of oils and greases the cleaning solution should have a relatively low surface tension. Unfortunately, solutions of most of the common alkalies have relatively high surface tensions, as can be seen from Table I.

TABLE I
SURFACE TENSIONS OF ALKALI SOLUTIONS

Alkali (2% solution)	Surface Tension (20° C) dynes per cm.
Water	72·8
Sodium hydroxide	77·0
Sodium carbonate	77·0
Trisodium phosphate	76·2
Sodium silicate	76·3
Sodium aluminate	75·6
Soap	28·0

It will be seen that a soap solution has a considerably lower surface tension than have solutions of alkalies; this is the case even when soap is present in very low concentration. For this reason soap is a very useful constituent of an alkaline detergent, and even when it is not deliberately added a certain amount of soap gradually forms in such detergents due to the saponification of oils and fats present on the parts being cleaned in them. This beneficial action of soaps has been recognised by electroplaters for a very long time and it used to be common practice to put a small amount of solution taken from an old cleaning bath into freshly made solutions.

As practical surface active materials soaps have definite limitations, however. In the first place, when used in hard water, they interact with the calcium and magnesium salts present in the latter giving insoluble precipitates. Thus, not only is the soap removed from the solutions but these precipitates may cause difficulties themselves if they are precipitated on to metal surfaces which are being cleaned, for example.

An even more serious limitation to which the soaps are subject is that at a pH of 10·2 or lower they begin

* *J. Inst. Electrodepos. Tech. Soc.*, 1944, 19, 131–146.
1 Foster Dee Snell, *Ind. Eng. Chem.*, 1943, **35**, 107

to decompose. Hence soap solutions cannot be employed where wetting properties are required in neutral or in acid solutions. This limitation is not of overwhelming importance with the stronger alkalies used in the cleaning of steel and brass. Where milder alkalies must be used, as when zinc or aluminium are being cleaned for instance, a pH of 9–10 should be aimed at, and the instability of soaps under these conditions makes it preferable to use other surface-active substances if it is desired to bring about a reduction in the surface tension of the cleaning solutions.

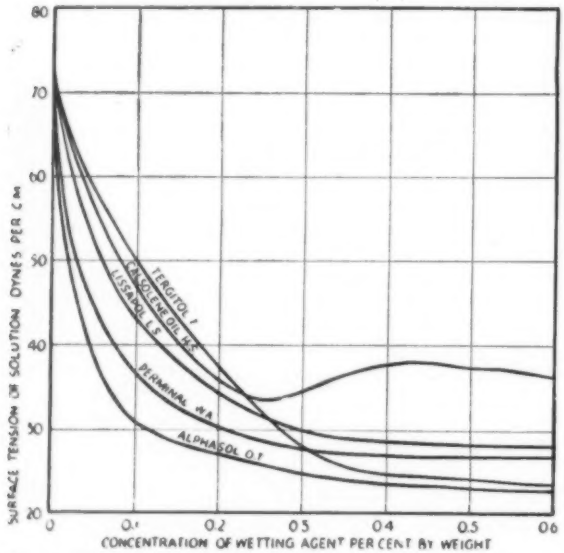


Fig. 1.—Effect of various wetting agents on surface tension of 4% caustic soda solution.

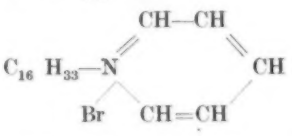
Sulphated Fatty Alcohols. The sulphated fatty alcohols constitute one of the most important groups of wetting agents ; they are produced from the long chain fatty alcohols and their advent to industry was a direct result of the development of the manufacture of these alcohols by the catalytic reduction of the fatty acids. Amongst the alcohols most generally used are lauryl and myricyl alcohols produced by the reduction and fractionation of coconut oil, and stearyl and oleyl alcohols obtained similarly from stearic and oleic acids respectively. Their structures are fundamentally very similar to that of the soaps, the main difference being that whereas in the former the active group is the sulphate group—$O.SO_2.ONa$, in the case of soap it is the sodium carboxylate group—COONa. The aliphatic sulphates are stable in hard water, are not hydrolysed in water and are active in neutral solutions. As the length of the carbon chain increases from C_{12} to C_{18} the wetting properties increase.

Aryl Alkyl Sulphonates. The aliphatic sulphonates have also been produced ; many of them are relatively costly to manufacture although some have excellent surface-active properties. Amongst the best known of these are the sulphosuccinic acid esters, which are commercially available. Alphasol OT for example, is the dioctyl ester of the sodium salt of sulphosuccinic acid.

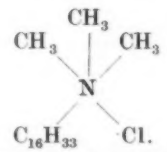
The aryl alkyl sulphonates, on the other hand, are the cheapest, and most readily manufactured of the surface-active compounds. They consist of an aromatic nucleus containing a sulphonate group (e.g., naphthalene is commonly employed) to which is attached an aliphatic hydrocarbon radical. The aromatic radicals may be hydrogenated and alkylated.

This group of compounds is characterised by stability in hard water and high surface tension depressing properties. Their detergent qualities are poor, however, and they do not foam readily.

Cation-Active Materials. The materials so far considered have been of the anion-active type ; in other words the larger portion of the molecule when ionisation takes place in solution is negatively charged. The main cation-active materials (in which the compound ionises so that the bulk of molecule becomes the cation) are typified by the quaternary ammonium compounds and the primary and secondary amine acid salts. The cation-active materials are specially useful in neutral or in acid solutions where they possess good detergent, peptising and emulsifying properties. One advantage of the cation-active materials is that the active ion cannot react with any heavy metal ions. Typical compounds of this type are :



cetyl pyridinum bromide



trimethyl cetyl ammonium chloride.

In addition to these there are also non-ionising surface active materials and these are particularly stable in acid solution, although they are rather lacking in detergent qualities. One such material is glycerol monostearate : $C_{17}.H_{35}.CO.O.\ CH_2.CH\ (OH)\ CH_2.OH$, produced by the condensation of gylcerine with stearic acid.

Petroleum Derivatives. Up till comparatively recently animal and vegetable fats were essential for the manufacture of surface-active materials, since it is from the natural oils and fats that the long-chain fatty acids and alcohols are obtained. Considerable quantities of surface active materials are now being made for detergent and other purposes from petroleum bye-products, and the production of these is wholly independent of natural fats.

The selected hydrocarbon fraction which is chosen is largely composed of oleines within the range of C_8–C_{18}. By treatment with sulphuric acid under controlled conditions the crude sulphated derivative is obtained and after neutralisation and purification a pale yellow liquid is produced which consists of a solution of the sodium salts of the corresponding secondary alkyl sulphates, together with a certain amount of sodium sulphate. This solution is marketed commercially and has many useful applications.*

Wetting Agents in Cleaning Solutions

One of the most important applications of wetting agents is in cleaning solutions. The alkalies employed in metal cleaning practice are relatively limited in number and each has its special characteristics. Commercial cleaners are therefore compounded from several alkalies to obtain the required results. Amongst the commonest constituents of alkali cleaners are caustic soda, sodium

* Known commercially as "Teepol"

carbonate, sodium silicate, trisodium phosphate and soap. Cleaners must be capable of saponifying vegetable and animal oil contaminants, i.e., combining with them to produce soluble soaps which can be readily rinsed away. Mineral oils cannot be saponified to any appreciable extent and when these are present the cleaner must be an effective emulsifying agent

A successful detergent must also be capable of peptising or dispersing the contaminant, preventing the recoalescence of the particles after they have been emulsified. It must also have good rinsing qualities. Surface-active materials can play a useful part in achieving these desiderata.

It has already been pointed out that solutions of most alkalies have relatively high surface tensions and so are defective in wetting properties which facilitate emulsification and peptisation of contaminants on metal surfaces by cleaning solutions. Soaps, which are commonly added to improve matters in this respect suffer from the limitations that they have relatively low solubility in cold water, are precipitated by calcium, magnesium amd heavy metal salts and are hydrolysed at pH values of less than 10·2. In the presence of any appreciable salt concentration they may also be precipitated with a further reduction in the amount of soap present. They are also not readily rinsed off after cleaning operations.

Low surface tension is not in itself sufficient to make a solution a good detergent, although it is an important contributory factor in obtaining good cleaning. A detergent must not only be capable of emulsifying and dispersing the contaminant, but must also be able to hold the material in suspension and prevent the reagglomeration of the particles. These dispersing properties vary considerably with different substances, and depend on the formation of an adsorbed film on the particles. Some alkalies (e.g., sodium silicate) have excellent dispersing properties despite the fact that the surface tension of their solution is relatively high.

According to Hartshorn[2], good detergent surface-active materials are characterised by relatively simple long-chain non-polar groupings with powerful polar groupings such as the sodium carboxylate group. The detergent properties of surface active materials will also be affected by the presence of other constituents of the detergent solution which may affect the pH or may facilitate the dispersion of the contaminating substance. It is worthy of note that the effect of increased temperature is generally to lower pH in alkaline solutions. Thus for 1% caustic soda solutions, an increase from 25° C. to 60° C. causes the pH to fall 0·94 pH unit, and for 1% sodium metasilicate 0·71 unit[3]. Only relatively low concentrations of wetting agents are needed to bring about the optimum reduction in surface tension. Fig. 1 shows the relation between surface tension and concentration for five different wetting agents in 4% caustic soda solution. Tergitol 7 is an alkyl compound in which the active sulphate group $-O.SO_3Na$ is attached to the middle of the molecule. It is represented by the formula :

$$C_1H_9.CH\,(C_2H_5).C_2H_4.CH(SO_4.Na)C_2H_4.CH(C_2H_5)_2.$$

Calsolene oil HS and Lissapol LS are of the sulphonated fatty alcohol type ; Perminal WA is an aryl alkyl naphthalene sulphonate whilst Alphasol OT is the dioctyl ester of the sodium salt of sulpho-succinic acid.

2 D. S. Hartshorn, Jnr., *Met Fin.*, 1941, **39**, 129.
3 L. E. Kuentzel, J. W. Hensley and L. R. Bacon, *Ind. Eng. Chem.*, 1943, **35**, 1280

Electrolytic Cleaners

In electrolytic cleaners the anionic or catonic nature of the wetting agent becomes important, and here two opposing factors come into operation. Clearly, a catonic material will be more effective if cathodic cleaning is in use and *vice versa*. On the other hand, the large non-polar cation may be precipitated on the surface being cleaned when its charge becomes neutralised and the film so produced may be difficult to remove. Many of those acids or sulphonic acids, the sodium salts of which are important surface active materials, are themselves insoluble.

It is also important to note that anion-active and cation-active materials should not be mixed, as this may result in the precipitation of an insoluble compound.

Foaming

Surface-active materials promote foaming due to the concentration of the wetting agent at the interface. Usually the foaming properties are a measure of the detergent qualities, i.e., the more detergent types of materials produce more foam than do those which are largely surface-tension depressants only. Foam formation is dependent on the presence of the appropriate concentration of surface active agents at the interface.

Capacity for foam formation is very dependent on the solubility of the material. If the surface area of the film is increased by agitation or by other means, the concentration of the active material in the interface is reduced and a state of dynamic equilibrium is reached when no further extension can occur. The stability of the foam and the amount produced are functions of the stage at which such equilibrium is set up. Excessive solubility of the surface-active material does not permit its migration into the interface. It will then tend to remain in solution only wholly in the aqueous phase and an insufficient concentration will exist at the interface for effective surface activity to manifest itself. Thus if a foam is produced on the surface of a solution of saponin it is found that the concentration of saponin in the foam differs considerably from that found in the interior of the solution. Moreover, if air is passed through such a solution and the foam is removed, after a certain time the residual solution ceases to have foaming properties whilst the liquid obtained by condensing the foam itself has considerably increased foaming powers.

Testing of Cleaners

The evaluation of cleaning solutions is not easily carried out. Perhaps the simplest method is to suspend a plate coated as uniformly as possible with oil in the detergent solution and to determine the time which elapses before the articles can be removed from the solution without evidence of a "water-break." More recently the use of an oil carrying a fluorescent dyestuff has been suggested.[4] After immersion in the cleaner for a given time, metal plates which have been coated with the oil are examined or photographed in ultra-violet light, the amount of fluorescence remaining being a measure of the thoroughness of removal of the contaminant.

4 O. M. Morgan and J. G. Lankler, *Ind. Eng Chem.*, 1942, **34**, 1158.

In some tests on these lines it was found that the addition of Nacconal NR (a long-chain alkyl aryl sulphonate) reduced the time required for the removal of oily contamination from metal surfaces very appreciably. Thus, using a 10% solution of a cleaner consisting of :

Caustic soda	10%
Trisodium phosphate	55%
Soda ash	35%

at a temperature of 140° F. fluorescence was still evident after ten minutes, showing incomplete removal of the oil. When 5% of the wetting agent was added to this mixture, however, a 2% solution effectively removed the oil.

Sodium metasilicate solution under similar conditions effects almost complete removal of the oil when it is used alone. On the other hand, 3 to 4% solutions of a cleaning compound containing 5% of Nacconal NR plus 95% of sodium metasilicate effected complete removal of the mineral oil in 2–4 minutes although a 14% solution of metasilicate alone did not achieve this in ten minutes. Experiments carried out on metals other than steel showed similar improvements ; the cleaning of aluminium and galvanised iron was especially favoured by the presence of the wetting agent, although the improvement was less marked with brass and with tin-plate.

Tests showed that it is necessary to use 10% of rosin soap in a cleaner to obtain an efficiency equal to that produced by a 5% concentration of Nacconol NR ; this applies in soft water only, since the wetting agent is unaffected by hard water.

Wetting agents are influenced by the nature of the alkali and the conditions of operation ; for maximum effectiveness the correct material to use must be carefully selected. Excessive concentrations should be avoided to prevent rinsing difficulties and only just sufficient should be used to bring the surface tension down to the required value. It is found usually that as the concentration increases the surface tension falls until a concentration of perhaps 0·2% is reached, after which further additions produce little change in surface tension and so are not of great value.

Pickling Processes

As has already been stated, the advent of the synthetic surface-active materials has enabled materials to be produced which are capable of lowering the surface tension of acid solutions and are stable in their presence.

The surface tensions of the usual pickling solutions consisting of 5–15% of hydrochloric or sulphuric acid are approximately equal to that of water. The addition of a wetting agent promotes more uniform contact of the pickling acid with the metal. The wetting-out action of acids on scaled metal surfaces is variable and is due in part to the presence of traces of oil which have not been properly removed in the degreasing operation which should precede pickling. Also, traces of carbonised grease produced during heat-treatment operations are sometimes present on the metal surface and these tend to make the scale not readily wetted.

For use in pickling solutions the wetting agents should be stable in the acid and should not be decomposed by it at the working temperatures employed (which may be as high as 180° F.) nor be reduced by the hydrogen evolved in the pickling operation. Highly surface active materials are strongly adsorbed at metal surfaces and they therefore tend to act as pickling inhibitors, reducing the action of the acid on the clean steel from which the scale has been removed and thereby saving both metal and acid.

Inhibitors

The wetting agents are not as effective from the purely inhibiting point of view as are the materials specifically developed for this purpose. These latter act either by adsorption at the descaled metal surface reducing the attack of the acid at the descaled areas or, according to other authorities, by increasing the hydrogen over voltage[5]. Hydrogen evolution is considered to take place preferentially at local inclusions and at grain boundaries of the metal which behave cathodically. The discharge of cations at these points inhibits the evolution of hydrogen and hence reduces acid attacks. Amongst the most effective inhibitors appear to be the heterocyclic nitrogen compounds such as pyridine and quinoline and their derivatives. Other effects, apart from wetting properties, enter into the requirements of inhibitors since these compounds would not be considered as effective wetting agents[6]. Nevertheless, wetting agents must not be too strongly adsorbed or used in excessively high concentrations since this may result in highly adherent residues being left on the metal surface, which may cause trouble during subsequent operations. Whilst the use of wetting agents does not eliminate the need for degreasing prior to pickling, it may enable more rapid and uniform pickling to be obtained in cases where complete removal of such grease is difficult, if not impossible.

Spot-Welding of Light Alloys

The recent development of the electric spot-welding method for the fabrication of aluminium and duralumin sheet has opened a further field for the application of surface-active materials. Before spot welding can be successfully carried out the sheet must be free from grease and must also be clean. The essential feature is that the surface of the material with respect to cleanliness and freedom from oxide should be uniform since the conditions of welding are themselves critical and any non-uniformity manifests itself in the form of irregular and poor welds. The use of relatively concentrated phosphoric acid solutions containing a wetting agent of the alkyl aryl sulphonate type has been recommended[8] as a pickle to obtain the required surface conditions. The phosphoric acid solutions of this concentration are relatively viscous and the wetting agent greatly facilitates uniformity and speed of pickling.

In some work carried out by the author more satisfactory results were obtained by the use of rather more

TABLE II

RELATIVE SURFACE TENSIONS OF FIXANOL C, PERMINAL WA AND PERMINAL COL IN 5% PHOSPHORIC ACID SOLUTION

Wetting Agent	Surface Tension dynes per cm.		
	5% H_3PO_4	After adding wetting agent	After 180 hours at 50° C
Fixanol C (0·1% W/V)	60	38	38 (clear)
Perminal WA (0·1% W/V)	60	32	32 (clear)
Perminal COL (0·1% V/V)	60	36	37 (cloudy)

5 Chappell, Roetheli and McCarthy, *Ind. Eng. Chem.*, 1928, **20**, 582.
6 H. Silman, *Sheet Metal Ind.*, 1943, **17**, 1022.
8 T. E. Piper, J. Am. Welding Soc., 1941, 661 ; H. O. Klinke, *ibid*, 1943, 602.

dilute phosphoric acid solutions (5–10%) at temperatures of about 50° C. It was found that the stability of most wetting agents in phosphoric acid maintained at 50° C. was only fairly satisfactory; after a time the solutions became cloudy, due to breakdown of the material with a tendency for the formation of a film on the surface of the sheet when the latter was withdrawn from the solution after pickling. The most satisfactory of the materials tested was Fixanol C, a cation-active compound; the relative stabilities of the three best wetting agents examined in 5% phosphoric acid are indicated by the figures given in Table II.

Electrodeposition

Much of the information available regarding the utilisation of surface active agents in electrodeposition is concerned with nickel plating. The object of their use in this case has been two-fold. In the first place it was desired to obtain a means of reducing the well-known tendency for "pitting" to occur in nickel plating solutions; secondly, the usefulness of such materials in the technique of bright nickel plating has been the subject of investigation. In some instances it has been found that surface-active materials which reduce surface tension also result in bright nickel deposits being produced under certain conditions, but this is by no means always the case. It is therefore difficult to treat these functions separately.

In a recent investigation[9] of the relative effectiveness of a number of different wetting agents in reducing the surface tension of a nickel plating solution of the usual type it was found that, of the materials tested the best were, in order of decreasing effectiveness:

Cetyl pyridinium bromide (a quaternary ammonium compound).
Lyofix DE (a quaternary ammonium compound).
Igepon T ($C_{17}H_{33}CO.NH.CH_2.CH_2.SO_3Na$).
Sapamine K.W.C. (a quaternary ammonium compound).
Nekal B.X. (1·4—isopropyl naphthalene sulphonic acid).

As expected, however, it was found that effectiveness from the surface-tension reduction point of view was not the only criterion of usefulness of the materials in nickel-plating solutions. Some of the wetting agents produced pitting or nodulation, whilst others (e.g., cetyl pyridinium bromide) resulted in a marked reduction of cathode efficiency. Of the materials examined only Igepon T produced entirely satisfactory deposits. These were dull, smooth, fine-grained compact, pit-free and strongly adherent; the smoothest deposits were obtained after the surface tension had been reduced to 38 dynes per cm. or less. The plating tests were carried out at a current density of 1 amp. per sq. dm. at temperature of 25°–28° C. without agitation.

The effect of the wetting agents, generally speaking, was to decrease the crystal size of the nickel; this decrease was greater the higher the concentration of the wetting agents. When the minimum surface tension was reached the crystal size was found to be smallest.

Bright Nickel Deposits

The advantage of bright nickel in that it eliminates the need for the polishing of the matt deposits obtained from the normal types of nickel-plating solutions has beeen widely recognised. A great many materials have been recommended as additional to such solutions, some of which are surface active agents, whilst others have no surface active properties. Foremost amongst the latter class are cobalt sulphate and sodium formate additions, and metallic brightening agents such as cadmium and zinc salts; these last-named are, however, little used in commercial practice.

One group of non-surface active materials which has been the subject of considerable investigation is that of aryl sulphonic acids, e.g., aromatic polysulphonates such as nickel benzene disulphonate and nickel naphthalene trisulphonate[10]. The absence of a long-chain aliphatic group accounts for the lack of surface activity, but these materials produce bright deposits. Not a great deal is known of the mechanism whereby this is brought about, but Hothersall and Gardam[11] have found that the microstructures of several types of bright nickel which were examined showed periodicity and evidence of a laminar structure. The inclusion of carbon in the deposit to the extent of 0·05–0·2% was also found, whilst sulphur has also been detected in some bright nickel deposits[12]. These effects point to the occlusion of the addition agent in the deposit. The grain size of the bright deposits is very fine, being in the order of 0·000004 in. or less.

Addition agents for use in nickel plating must be very carefully selected and in some respects the selection is empirical owing to the absence of a detailed knowledge of many of the factors involved. Some addition agents not only reduce current efficiency but also make the bath especially susceptible to impurities or reduce the corrosion resistance of the deposit. The latter is a most important consideration. Certain addition agents which are not surface active have been shown to produce a deposit having a minute micro-porus structure which results in poor corrosion resistance. By the addition of wetting agents this micro-porosity has been reduced in some cases. Dual addition agent systems consisting of a brightening agent in conjunction with a wetting agent are in commercial use. The range of materials which can be used in bright solutions is limited owing to the critical nature of the conditions required for bright deposits to be obtained; in the main the materials employed have been largely of the straight chain aryl alkyl sulphonate or alkyl sulphate types. One requirement is that the compound selected should have a nickel salt which is soluble within the pH range to be employed. It should, moreover, be stable in the solution.

The use of wetting agents in nickel solutions is therefore not free from dangers. The increase in the emulsifying and peptising properties of the plating solutions containing them also means that any organic materials and impurities generally tend to become dispersed in the bulk of the solution instead of remaining on the surface whence they can be easily removed. These impurities can originate from various sources.

Tin Plating

The acid tin-sulphate solution has also been a fruitful field for experiment with surface active materials and addition agents. Tin as deposited from a sulphate solution without the presence of an addition agent is

9 F. F. Davis, K. M. Wolfe and W. G. France, *Ind. Eng. Chem.*, 1941, **33**, 1546.

10 M. Schlötter: U.S. Patent 1,972,693 (1934).
11 A. W. Hothersall and G. E. Gardman, *J. Electrodepos. Tech. Soc.*, 1939, **15**, 127.
12 W. L. Pinner, G. Soderberg and E. M. Baker, *J. Electrochem. Soc.*, 1942, (Special Vol., 243).

crystalline and poorly adherent. Additions of beta-naphthol and cresol sulphonic acid are commonly used. More recently, however, additions of sulphated fatty alcohols together with quinol and cresylic acid have been proposed[13], as have also the use of tin benzene disulphonate acid with the addition of materials such as glue, gum, benzoin, etc.[14] For the stannous fluoborate bath the addition of aloin (a glucoside) has been recommended[15]. These latter materials are, however, either not surface active at all or have only slightly surface active properties.

Wetting agents have been used to a limited extent in acid and cyanide copper plating solutions and also in zinc and in brass solutions, but the results obtained have been variable and these additions do not at present seem worth while.

13 U.S. Patent 2,274,963.
14 M. Schlötter: U.S. Patent 2,271,209.
15 British Patent 552, 982.

English Steel Corporation Ltd.

Management Changes

IMPORTANT changes, which took effect from September 30th, have been made in the directorate of the above Corporation. Sir Charles Craven, Bt., chairman, has decided to relinquish the office of managing director, and is succeeded in that position by Sir Alexnder Dunbar. Sir Arthur Winder has resigned his position as director and general manager of the English Steel Corporation, Ltd., the Darlington Forge, Ltd., and Industrial Steels, Ltd. Mr. F. Pickworth, who is a director of these three companies, has been appointed general manager.

Sir Charles Craven, who is deputy chairman of Vickers Ltd., chairman and managing director of Vickers-Armstrongs, Ltd., and a director of other important concerns, became managing director of the English Steel Corporation in 1932, and in 1935 was appointed chairman.

Sir Arthur Winder has a great reputation as a steel-maker and is one of the few men in the country, working his way up through various stages to the position of first hand melter, has attained such eminence in the steel industry. He started work in the casting pit of the Siemens open hearth department of Thomas Firth and Sons, Ltd., and in his spare time studied metallurgy under Professor Arnold at Sheffield Technical School (now Applied Science Department of Sheffield University), gaining the Mappin Medal for honours in metallurgy and becoming an Associate of Metallurgy.

In 1906, Sir Arthur became manager of the new Siemens plant put down by Jones and Culver, Ltd., Realising from his own experience the impossibility of men maintaining good health and efficiency, when working 12 hours a day under hard manual conditions, he introduced the 8-hour day in the Siemens department six years before it became general throughout England.

In 1918 Sir Arthur returned to Thomas Firth and Sons, Ltd., as head of the steel melting departments, later becoming general manager and director of Industrial Steels, Ltd., a position he held until 1932 when he was appointed works director of all the Sheffield works of the English Steel Corporation, Ltd. He is a member of the Council of the British Iron and Steel Federation, a Fellow of the Royal Society of Arts, a searcher of the Cutlers' Company, a J.P. for Sheffield, and was for several years chairman of the Alloy Steels Association.

Sir Alexander Dunbar, the new managing director, was appointed commercial manager and special director of the English Steel Corporation in 1932; in 1933 he became a director and joint managing director in 1936. In the following year he was appointed to the board of Vickers-Armstrongs, Ltd. In 1938, he left Sheffield to become chief of the aircraft side of Vickers, having previously spent seven years in the aircraft industry.

For a period during the present war Sir Alexander, whose knighthood was announced in the New Year Honours List of 1943, served at the Ministry of Aircraft Production, first as Director-General of Materials Production, then as Deputy Controller-General, and later as Controller-General, and a member of the Aircraft Supply Council. He is a director of several companies, mostly concerned with heavy industry.

Mr. F. Pickworth, the new general-manager, joined the accountancy staff of Cammell Laird & Co. Ltd., in 1911. In 1915 he went to Nottingham as chief accountant of one of the first projectile factories erected for the Government, and in 1927 returned to Cammell Laird and Co. as assistant chief accountant. Later that year he was appointed chief accountant. On the formation of the English Steel Corporation in 1929, he became assistant secretary, and was made secretary in the following year, afterwards becoming a special director. Since his appointment as a director in 1936, Mr. Pickworth has been in control of finance and administration and of the planning, construction, and modernisation of works and plant, including large extensions on behalf of the Government, and from the beginning of the war he has also had charge of the sale organisation. In 1940, he was made a director of Vickers-Armstrongs, Ltd.; he is also a director of Firth-Vickers Stainless Steels, Ltd., Taylor Bros. and Co. Ltd., and the Oughtibridge Silica Firebrick Co. Ltd.

Flight Schedules and Fares for Pan-American Airways World Service in 1948

THE publication* of this hypothetical time table is of interest in showing that this company hopes to operate as an individual airline after the war and that considerable thought is given in the U.S.A. to these international developments.

The following are some excerpts :—

New York to—	Express		Local		Fares $	
	Daily Flight	Hours in Flight	Daily Flight	Hours in Flight	One Way	Round Trip
London	5	13·48	2	16·30	103·50	186·30
Paris	5	15·00	2	17·50	112·50	202·50
Berlin	5	16·00	2	19·12	120·00	216·00
Rio	10	19·00	5	22·48	142·50	256·50
Moscow	5	19·12	2	22·51	144·00	259·20
Buenos Aires	10	21·36	5	26·03	162·00	291·60
Cairo	3	23·12	2	24·44	174·00	313·20
Tokyo	2	27·36	2	33·03	207·00	373·60
Bombay	3	32·00	2	39·40	240·00	432·00
Capetown	3	34·00	2	41·20	255·00	469·00
Auckland	2	37·36	2	45·23	282·00	507·60
Sidney	2	42·00	2	50·40	315·00	567·00
Singapore	2	43·00	2	52·10	322·00	580·00
Hongkong	2	44·00	2	53·20	330·00	594·00

The Express Service will have the minimum of stops, whilst the " local " will call at intermediate ports.

The fares apparently refer to the express service—The relatively small reduction on returns should be noted.

* *Inter Avia*, No 927–928, June 28, 1944, pp. 25, 26

Courtesy of R.T.P. 3, Ministry of Aircraft Production.

Reviews of Current Literature

Colorimetric Determination of Traces of Metals

THE increasing importance of trace elements in a great variety of materials has led in recent years to great developments in the methods for their determination.

There are few things in inorganic analysis more satisfying than an elegant and accurate colorimetric method, but it is not sufficiently realised how solid a foundation of analytical skill and experience is required for success in this fascinating field. New reagents continually appear, and are enthusiastically described in the literature, but in many cases it must be confessed that enthusiasm has outstripped discretion. For example, the highly important question of interference by elements other than the one to be determined has only too often been imperfectly studied, and the unsatisfactory statement is often made that certain substances " interfere and must be removed." Having regard to the fact that the sample under examination may consist of such diverse matter as ferrous or non-ferrous alloy, soil, water, silicate rock, biological material, etc., the most important consideration usually lies in the actual " collection " of the trace metal, so that the preliminary work is of the greatest importance, and may call for analytical skill of the highest order.

These essentials are fully realised by the author of this book, which forms Vol. III of a series of monographs on analytical chemistry and its applications.

The principles of trace determinations are fully discussed, and excellent descriptions are given of the physical methods employed. Reagents of fairly general application are given a separate chapter, and this is followed by the detailed treatment, by selected methods, of the metals, in alphabetical order. Due regard is paid to the analytical chemistry of the metal (for upon this rests the most convenient way of separating it from undesirable and interfering elements) and a great deal of experimental data is given, involving such important points as degree of conformity to Bees' Law, etc.

The analyst confronted with the determination of trace metals will not find all his problems solved in this book, but he will find a wealth of invaluable information, which will usually enable him to develop a satisfactory solution.

It is a conventional compliment to say that the volume under review " should be on every chemist's bookshelf." It is a safe forecast that this excellent book, once purchased, will more often be found upon his desk.

By E. B. Sandell, Ph.D. Interscience Publishers, Inc., New York, 1944, pp. 487. 9 in. × 6 in. 42s. net. (Imperial Book Co., 1, Bloomsbury Street, London, W.C. 2.)

Further Experiments on the Damping Capacity of Metals

THIS is a reprint in convenient form of a paper recently read before the North-East Coast Institution of Engineers and Shipbuilders in Newcastle-on-Tyne. The work described was carried out in an effort to overcome difficulties experienced by the presentation of an earlier paper on the subject to this Institution, and to fill any additional gaps in knowledge which had become apparent. The subjects discussed can be arranged in a series of groups, according to the aspect of damping capacity to which they are most closely related. Thus, the first group embraces the factors which influence damping capacity ; the points of the second group deal with variations in the test conditions ; the third category deals with long-time testing ; while in the fourth group is an explanation of the marked difference between two steels discussed in the previous paper.

The experiments described in this work were carried out on specimens $9\frac{1}{2}$ in. long with ends $\frac{1}{2}$ in. square, a 2 in. gauge length of $\frac{5}{16}$ in. diameter being provided over the central portion. The top end of the specimen is clamped rigidly, whilst the bottom is fitted with a cross bar by means of which an initial twist can be given to the system prior to release. The amount of this twist is adjusted to produce a certain maximum surface stress S on the cylindrical surface of the specimen, the cross bar being held in the required position by means of a powerful electromagnet. On opening the circuit the specimen undergoes torsional vibrations of gradually decreasing amplitude which are recorded optically.

The specific damping capacity R is defined as the ratio of the loss of energy per cycle to the energy at the start of the cycle, i.e.,

$$R=\frac{a^2-b^2}{a^2}$$

where a and b are the magnitudes of successive swings.

Tests were carried out on 66 specimens of various materials including steel, cast iron, light alloys and bakelite, the damping capacity R being tabulated for a series of maximum stresses ranging from 2 to 5 tons per sq. in. for steel and heavy alloys to a few hundred pounds in the case of plastic materials. By surrounding the specimen with an electrically heated tube furnace, the variation in damping with temperature of the material could be investigated.

The main results obtained from the experiments may be briefly summarised as :—

1. *Normalised Carbon Steels.*—The damping capacity R at 20° C. + S=2 tons per sq. in. ranges from 1 to 2%, depending on composition. Increasing S to 5 tons per sq. in. roughly doubles the damping capacity. In the case of mild steel, R at 500° C. is 3 to 6 times the room temperature value. With higher carbon content, the same temperature rise produces either a small positive or negative effort.

2. *Alloy Steels.*—R at 20° C. (S=2) is less than 0·5% and R at 600° C. (S=2) 1 to 3%. Increasing S to 5 tons per sq. in. raises R $1\frac{1}{2}$ to 2 times.

3. *Corrosion- and Heat-Resisting Steels.*—Ferritic stainless irons and steel have high damping capacity ranging from 2 to 8%, whilst R for the austenitic steels is less than 0·5 %. The damping of the latter is also affected to a less extent by temperature or stress than in the case of ferritic base materials.

4. *Cast Iron.*—This material has a very high damping factor ranging from 6 to 20% depending on composition and stress range.

5. *Nickel.*—R diminishes from 10 to 0·6% as the temperature is raised to 500° C. Increase in S causes R to diminish.

6. *Cobalt.*—R increases from 0·7 to 10% as the temperature is raised to 470° C. Increase in S causes a marked increase in R.

7. *Light Alloys* (*room temperature*).—In the case of aluminium base alloys, R is affected very little by the stress S. For magnesium base alloys there is an appreciable increase in R for the higher stress values.

8. *Bakerlite* (*room temperature*).—R varies from 20 to 25% depending on stress ranges and composition of plastic.

9. Damping coefficient of miscellaneous materials (room temperature). Lead 20 to 30%. Glass 2%. Copper alloys 0·5%. Ivorine 30 to 50%.

The authors point out that the variation of the damping coefficient with temperature and stress is evidently connected with changes in the internal structure of the material and may thus serve as a useful tool for general material research.

The book contains 58 pages ($9\frac{1}{2} \times 6$ in.) inclusive of bibliography and discussion and is a very important contribution to the subject of damping capacity of materials.

By the late W. H. Hatfield, D.Met., F.R.S., L. Rotherham, M.Sc., F.Inst.P., and Miss E. M. A. Harvey, M.A., B.Sc. Published by the North-East Coast Institution of Engineers and Shipbuilders, Bolbec Hall, Newcastle-on-Tyne.

Boiler Blow-down

THERE is surprising ignorance about boiler blow-down ; why, when, and how much is necessary. The general impression is that boilers are blown down simply to blow out sediment and mud from the bottom of the shell or drums ; and that by blowing down, scale is lessened.

Little is known about the safe limits of concentration of the salts in the boiler water in relation to priming. The hydrometer is regarded as a scientific instrument only to be handled by the chemist. Even when a chemist is employed, would it be true to say that his reports are understood

Undoubtedly, there is much about boiler blow-down which so far has been a " closed book " to many works engineers and boilerhouse men. Much depends upon correct blow-down conditions and some authoritative guidance on the subject is timely. This guidance is offered in a new Bulletin issued by the Ministry of Fuel and Power, and every steam-boiler user will find it to be of the greatest benefit.

The Bulletin begins by explaining why blow-down is necessary. Having made that point clear, it gives a useful guide as to the best time to blow down. It then proceeds to describe the routine control of blow-down and to examine the factors which influence the amount of blowing down necessary to prevent priming. The value and use of the hydrometer in testing samples of boiler water to ascertain the amount of dissolved solids it contains is dealt with at length. The need for careful supervision where continuous blow-down is fitted, in order to prevent unnecessary loss of heat (and fuel), is stressed. Then follows a section on heat recovery from continuous blow-down. Much has yet to be done in this direction as a source of fuel saving. It would be true to say that there are still many steam-boiler users who do not realise that they have in their boiler blow-down much useful heat that can be put to work and so reduce the amount of heat to be provided by the boilers. The bulleting also gives very clear directions for calculating the amount of blow-down required, and the information will go a long way to clear up doubt which exists on this point.

The Bulletin is available free of charge from the Ministry of Fuel and Power, London, or from Regional Offices of the Ministry.

Lanthanum

Some of its interesting Properties

Lanthanum is the most electropositive of the rare earth metals groups. It was discovered by the Swedish scientist, Carl Gustave Mosander in 1839 in the nitric acid extract of a sample of ceria. Since the new metal had previously escaped detection Mosander named it lanthanum after the Greek *lanthano*, " be hidden." Recent studies indicate that lanthanum is more common in the earth's crust than at least 50 other of the known 92 elements.

Lanthanum occurs in a dozen different minerals such as cerite, parisite, and monazite, usually associated with cerium. The mineral is finely ground and extracted with acid, usually hot sulphuric acid and hot hydrochloric acid. Mosander had used nitric acid. For a number of years, during the Welsbach mantle era, pure lanthanum salts were prepared by the fractional crystallisation of the double nitrate of lanthanum and magnesium.

F. Trombe of Paris [Trans. Electrochem. Soc. 66, 59 (1934)] recommends the following procedure for the preparation of lanthanum metal : A graphite crucible to serve as anode and a rotating molybdenum rod as cathode. The fused electrolyte (850° C.) is composed of 25 g. $LaCl_3$, 16 g. KCl, and 2 g. CaF_2. The cathode current density is 4 amp./cm² at 7 volts. The current efficiency is approximately 65%. Samples of the metal contained 0·05% Si and 0·006% Fe ; spectrographic examination revealed absence of calcium and aluminum. B. S. Hopkins and L. F. Andrieth [Trans. 66, 135 (1934)] prepared lanthanum amalgams upon electrolysis of saturated ethyl alcohol solutions of $LaCl_3$ using a mercury cathode. A pasty mass containing 1 to 3% La was obtained.

Lanthanum metal is ductile and as white as tin. The specific gravity is 6·92 and the melting point 815° C. (Ce. 623°). The atomic number is 57 and the atomic weight 138·92. Lanthanum, like cerium, adsorbs hydrogen readily. The compound LaH_3 is known.

The chloride and nitrate are very soluble but the sulphate is the least soluble of the rare earth group sulphates. Lanthanum salts are colourlesss. W. R. Mott, in his classical researches [Trans. 37, 689 (1920)], studied the arc image of La_2O_3 and found it to comprise a blue arc core, a dark inner layer between core and shell, and a yellowish-green arc shell, a combination of arc shell layers produced by no other element.

The well known " flints " for cigarette lighters are brittle alloys of iron, cerium and lanthanum in varied proportions. La forms solid solutions with magnesium but not with aluminium. La_2O_3 is a constituent of certain ceramic glazes and optical glasses. The interesting properties of lanthanum are an invitation to research in the field of alloys, vacuum tubes, electro-co-deposition, etc.

C. G. F. in August, 1944, issue of the *Bulletin of the Electrochemical Society*.

MICROCHEMISTRY
APPARATUS · METALLURGICAL APPLICATIONS · TECHNIQUE

SEVERAL of our contemporaries have recently stressed the necessity for urgent steps to improve the position of the publishing trade. While official publications are still taking a very large share of the necessarily reduced paper stocks, publishers are receiving a quota of paper which is totally inadequate for immediate and future needs, compared both with that available to the Government and with that used by American publishers. Scientists of all ranks must be especially alive to the seriousness of the position. New scientific books either are not published at all in this country or appear in small and therefore wasteful editions. Standard works are being used up more rapidly than they are being reprinted. For the experienced worker in analytical chemistry at the present time standard works are either difficult to obtain or, in many cases, obsolescent. Advances in technique, such as those with which we deal in these columns are not, in general, available in book form, although many of these advances may now be judged to have become a part of recognised practice. The student is in no better case, since text-books in analytical chemistry, as in other branches of chemistry, are reported, one after the other, regretfully out of print. Before long we will find ourselves dependent for our up-to-date literature on our Allies across the Atlantic. The cloud is much bigger than a man's hand. It is more than time for avoiding-action.

The Application of Diffusion to Micro-Analysis

By G. H. Wyatt, Ph.D., F.R.I.C.

Early work on the identification of gases on the micro scale made little use of the principles governing diffusion, and experiments to extend the methods to quantitative analysis were not at first very successful. Attention to the proper design of apparatus, however, has made possible accurate quantitative diffusion analysis with minute amounts of evolved gases.

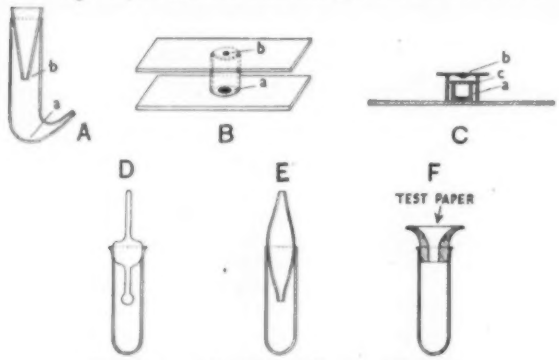
IN spite of Graham's distinction between crystalloids and colloids by the much more rapid diffusion of the former, one is apt to think of the process as being a slow one both in gaseous and liquid phases. Moreover, earlier attempts to apply diffusion methods to chemical analysis confirmed this impression—for example, Schlösing[1] and Shaffer[1] some 30 years ago attempted to estimate ammonia by diffusion from one vessel into another containing an absorbent, both vessels being placed under a bell-jar; they found that from two to four days were necessary, but that even then the results were somewhat low. However, the following account will show that, by the use of suitably designed apparatus, the method is not only applicable on the micro scale, but is also rapid, convenient and accurate.

If it is wished merely to identify a gas or vapour, quantitative absorption is unnecessary, although if this does not occur the sensitivity of the method will be reduced. As early as 1887, Rössler[2] found that by use of the apparatus (A, Fig. 1) it is possible to recognise 0·02 mg. CO_2. He placed the sample (minimum 0·05 gm.) at *a* and suspended a drop of baryta water at the base of the upper tube *b*, the outer tube being then dipped in acid. Rössler also used this apparatus for the detection of sulphite by iodine-starch solution, nitrate by ferrous sulphate solution, nitrite by potassium iodide, sulphide by lead acetate, and ammonium salts by copper sulphate.

Various modifications of this apparatus have been proposed, the simplest possibly being that due to Molisch[3] and described by Emich[4]; it consists of two microscope slides separated by a cylinder cut from glass tubing, the ends of which are ground plane and parallel (B, Fig. 1); the upper slide may be replaced by a cover slip. The reaction is carried out on the lower slide *a* and a drop of the detecting solution *b* is suspended from the upper. Molisch identified ammonia by formation of the octahedral crystals of the chloroplatinate, whereas Mayrhofer[5] suggested Nessler's solution, mercurous nitrate, dilute HCl or iodic acid as alternatives. Mayrhofer also improved the diffusion cell by introducing a small glass

1 E. J. Conway. *Micro-diffusion Analysis and Volumetric Error*. London, 1939.
2 O. Rössler. *Ber.*, 1887, **20**, 2629–31.
3 H. Molisch. *Mikrochemie der Pflanze*. Jena, 1921, p. 65.
4 F. Emich. *Microchemical Laboratory Manual*, transl. F. Schneider, New York, 1932.
5 A. Mayrhofer. *Mikrochemie der Arzneimittel und Gifte*. Vienna and Berlin, 1923-8, (vol. I, pp. 6–8).

capsule *a* (C, Fig. 1) to contain the reactants, spray from which was prevented from reaching the hanging test solution *b* by a glass plate *c* having four holes for the passage of the gas or vapour ; other authors recommend a piece of filter paper for this purpose. Emich (loc. cit.) also suggested that the gas should be liberated



Figs. 1.—Cells for qualitative diffusion analysis.

in a small test-tube which is closed by a cork carrying a platinum wire loop to hold the absorbing solution. Feigl and Krumholz[6] used a similar arrangement (D, Fig. 1), in which the cork is replaced by a ground joint and the wire loop by a glass tube ending in a small bulb. Feigl[7] also described several other variants of this apparatus ; in connection with the obvious replacement of the ground joint by a rubber bung, he suggested filling the bulb with magnesia or plaster of paris to render coloured reaction products easier to see. E, Fig. 1 is a form somewhat resembling Rössler's, which is due to Feigl (loc. cit.), while F, Fig. 1, is adapted to the recognition of gases or vapours by their action on test papers which are laid on the small ground-in funnel. The use of such apparatus has been greatly extended by Feigl and his collaborators,[7] who describe many inorganic and organic applications.

Emich[4] pointed out that if a drop of solution is to be treated with a gaseous reagent (e.g., bromine, ammonia, etc.) it is sufficient to place the test solution on a slide (as at *b*, B, Fig. 1) and to place the slide on the open mouth of an ordinary reagent bottle containing a solution of the reagent. Toms,[8] however, recommended the apparatus of Fig. 2 for the micro-determination of the iodine value of an oil by measurement of the gain in weight in bromine vapour. The oil is spread in a thin

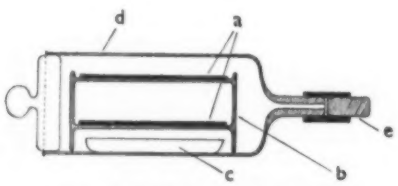


Fig. 2.—Cell for iodine value determination.

film on microscope slides *a*, supported on a glass cradle *b*, which is placed in a stoppered tube *d* ; a small boat *c* contains bromine. After exposure for 20–30 mins., the excess bromine is drawn off by removing the glass plug *e* and connecting to a filter-pump, the stopper being withdrawn. The gain in weight of the film—i.e., the bromine absorption—is converted into the iodine value by the factor 1·588 (= at. wt. of iodine/at. wt. of bromine). An indication of the identity of the oil may also be obtained from the appearance of the brominated film.

A cell similar to those of Fig. 1 (A, D, E, F) has also been used for quantitative analysis by Bentley and Kirk,[9] whose apparatus is shown at A, Fig. 3. These authors determined organic nitrogen by the Kjeldahl method, the solution resulting from the digestion being transferred to the small conical flask *a*, which is closed by a stopper carrying a hook *b* upon which is hung a capsule *c* containing the standard acid ; the caustic-soda solution is added in a second capsule *d*, which stands on three feet and which is upset when the liberation of ammonia is desired. 5 γ nitrogen may be absorbed in about two hours. "Creeping" of the acid solution up the walls of the flask causes a low result, as some of the ammonia then remains unattacked by caustic alkali ; this is avoided by wiping round the flask wall with a cotton-wool pad soaked in caustic-soda solution, so forming a ring of alkali. Tompkins and Kirk[10] performed a complete Kjeldahl determination (1 — 20 μ g. N) without transference in the special cell B (Fig. 3), designed for the purpose. Decomposition by sulphuric acid is effected in the bulb *a*, the tube being held vertically and the stopper withdrawn ; the ammonia is then liberated by alkali, the stopper being inserted and

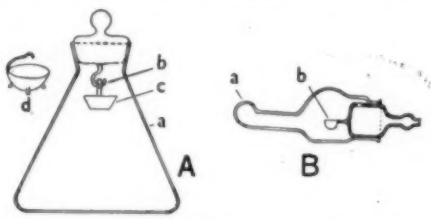


Fig. 3.—Cells for Kjeldahl determination.

the ammonia absorbed in the capsule *b*, the apparatus being horizontal, as shown ; the diffusion may be carried out *in vacuo*. A similar apparatus was also described by these authors, the ground joint being replaced by a cork.

The fundamental principles of the micro-diffusion method have been considered in detail by Conway,[1] whose book on the subject also describes many biochemical applications and gives references to the literature. In general, the process takes place in stages : (1) Diffusion of the volatile component from the bulk of the solution to the surface, where it (2) volatilises and is (3) transferred to the surface of the absorbent ; (4) it is then absorbed. Mathematical consideration of these factors led Conway to a design for an efficient unit for quantitative micro-diffusion analysis. This unit (A) is shown in Fig. 4 ; it consists of a moulded "Pyrex" glass lower part which may be considered as a Petri dish with an inner circular wall about half the height of the side. The upper part is a square glass sheet ground on one side to fit the ground top of the outer wall of the

6 F. Feigl and P. Krumholz. *Mikrochem.*, Pregl. Fest., 1929, **83**.
7 F. Feigl. *Qualitative Analysis by Spot Tests, Inorganic and Organic Applications*. Transl. J. W. Matthews. Amsterdam, 1937.
8 H. Toms. *Analyst*, 1928, **53**, 69 ; 1936, **61**, 177–8.
9 G. T. Bentley and P. L. Kirk. *Mikrochem.*, 1937, **21**, 260–7.
10 E. R. Tompkins and P. L. Kirk. *J. Biol. Chem.*, 1942, **142**, 477–485.

lower part, vaseline being used to effect a seal. The volatile constituent is liberated in the annular space between the two walls, and is absorbed in the inner compartment. It is evident that for maximum speed of operation the surface areas of the solutions should both be as great as practicable, not only to form large evaporating and absorbing surfaces, but also to minimise diffusion of the volatile constituent from the bulk of the solution to the surface. An opposing factor is that the mean molecular path of the volatilised substance should be a minimum if diffusion in the gaseous phase is to be as rapid as possible. The unit is designed to afford the best compromise and is intended to hold about 1 ml. absorbing liquid and 0·1–2·0 ml. in the outer chamber. Conway has investigated, experimentally, the most favourable conditions for the analysis of various substances in the unit, as an example the estimation of ammonia may be selected for description. 1 ml. of standard acid (N/150 — HCl containing Tashiro's indicator*) is measured into the inner chamber and a known volume of the solution to be tested is pipetted into the annular chamber; the cover is placed on the unit leaving a small opening through which an excess of alkali solution is added to the outer chamber by means of a pipette. The unit is then completely closed and is set aside for two hours at ordinary temperatures for absorption to occur. The acid in the central chamber is finally titrated with standard baryta solution *in situ*. These conditions are suitable for the estimation of more than 14 γ ammoniacal nitrogen and must be varied if smaller amounts are to be determined. The alkali used for the liberation of the ammonia is a saturated solution of potassium carbonate, since of the commonly available alkalies this produces a solution with the greatest vapour pressure of ammonia; for strongly acid solutions containing ammonia, potassium metaborate is most suitable as evolution of CO_2 is then avoided. For

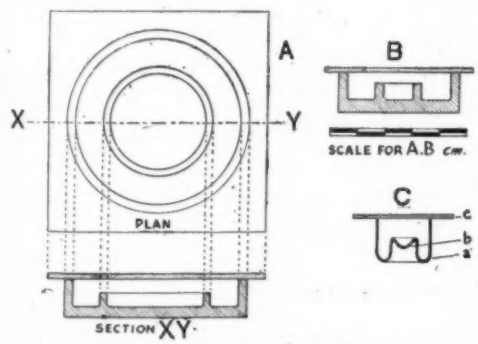


Fig. 4.—Conway diffusion units.

ammonia the time-absorption relationship is given by—

$$\frac{1}{t} \log \frac{a}{a-x} = A,$$

in which a is the initial ammonia concentration and x is the amount which has diffused after a time t; A is the "diffusion coefficient," which for ammonia at 20° C. has the value $1{\cdot}09 \times 10^{-3}$ cm²/min. The absorption time may be reduced by placing the unit in an incubating oven at 38° C., when the cover is sealed with a mixture of three parts vaseline melted with one part paraffin wax (m.p. 55° C.). The substance absorbed in the central chamber may also be estimated by colorimetric or other suitable methods. A smaller unit (B, Fig. 4) has been described by O'Malley, Conway and Fitzgerald,[11] which is particularly useful for CO_2 determinations; rates of absorption are comparable with those obtained with the original unit. An important feature is the improved seal against atmospheric CO_2, which is afforded by the thicker cell wall.

The Conway unit has been modified by Gibbs and Kirk[12] for use on the "drop scale"; the smaller cell (C, Fig. 4) is made from glass tubing *a*, the closed end of which is heated in the blow-pipe flame and sucked in; the central portion is then heated in a finer flame and is blown out to form a small cup *b*. The top of the cell is ground plane and is covered by a piece of ground glass *c*, which is sealed by a vaseline-wax mixture. Other modifications of the Conway unit are due to Bandemer and Scheibe[13] and to Prater, Cowles and Straka,[14] who could not obtain the original units. (They may be purchased without difficulty in this country.) The former improvised with a Petri dish and a glass ring fixed therein by de Khotinsky cement, which must be protected from alkali by beeswax. The latter imitated the Molisch cell, using 10 × 50 mm. or 15 × 100 mm. Petri dishes in which the ammonia was liberated; it was absorbed in a saturated solution of boric acid in glycerol, 5 or 13 drops of which were placed on a flat glass cover. After three hours' absorption at room temperature, the drops of acid were rinsed into a small flask for titration.

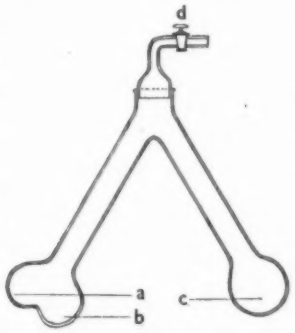


Fig. 5.—Diffusion cell for reduced pressures.

As already mentioned, the diffusion process may be accelerated by warming; it is also more rapid if conducted under reduced pressure, and if the ammonia, say, is absorbed in a cooled acid solution. These principles have been applied by Balachowski and Bruns[15] in the apparatus shown in Fig. 5, which was designed for the estimation of ammonia resulting from the Kjeldahl process. The sulphuric acid decomposition solution is placed in the bulb *a*; the adjacent bulb *b* contains the excess caustic-soda solution for the liberation of the ammonia, while the standard acid for its absorption is measured into bulb *c*. The apparatus is evacuated and the tap *d* closed; the contents of bulbs *a* and *b* are then mixed by tilting the apparatus. During the diffusion (about 15–30 mins.) bulbs *a* and *b* are placed in a water-bath at 30°–40° C. and *c* is cooled.

Allied methods which, however, fall outside the scope of this review, consist of the absorption of gases and vapours by bubbling through suitable solutions or by

* To 200 mls. of a 0·1% alcoholic solution of methyl red, add 50 mls. of a 0·1% solution of methylene blue. The colour change is red (acid) to green (alkali) at pH = 5·5.

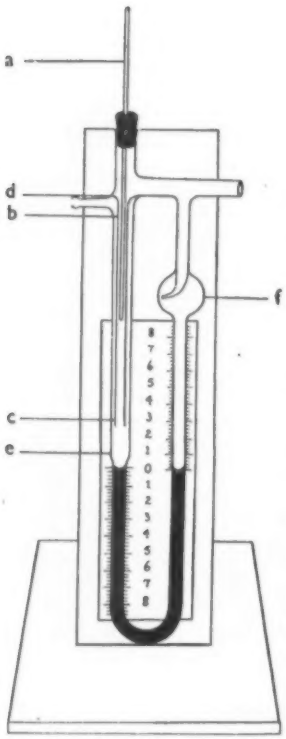
11 E. O'Malley, E. J. Conway and O. Fitzgerald. *Biochem. J.*, 1943, **37**, 278–281.
12 G. E. Gibbs and P. L. Kirk. *Mikrochem.*, 1935, **16**, 25–36.
13 S. L. Bandemer and P. J. Scheibe. *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 201–3.
14 A. N. Prater, E. J. Cowles and R. P. Straka. *Ind. Eng. Chem.* (*Anal.*), 1942, **14**, 703–5.
15 S. Balachowski and B. Bruns. *Biochem. Z.*, 1932, **256**, 292.

passing over solid absorbents, also the separation of a volatile constituent of a mixture by steam distillation or by ordinary distillation. For a full account of the theoretical and practical aspects of quantitative micro-diffusion methods the reader should consult Conway's book,[1] although, unfortunately, it is at present out of print.

I wish to thank Prof. E. J. Conway for permission to publish Fig. 4 (A, B), the units being registered designs, and to quote his findings.

The White-Wright Flowmeter

By R. Belcher, F.R.I.C.



IN all determinations where it is necessary to combust the sample under test in oxygen it is desirable to have some means of measuring the rate of oxygen flow, whether the analysis is on the macro or micro scale. In the original Pregl methods for determining the various elements in organic compounds, the flow was measured by means of a bubble counter calibrated with a Marriotte bottle. Later workers have recommended various types of flowmeter which afford a more convenient means of measurement. The bubble counter is, however, still widely used, and it is of interest to note that it is retained in the standard specifications recently drawn up in the U.S.A.,* whilst no provision is made for a flowmeter.

The writer has found the White-Wright design† the most convenient of the several types of flowmeter available. It has been referred to in several publications from his laboratory, and in consequence a number of requests for more detail has been received. Since this flowmeter does not appear to be as widely known as it deserves, the following description—which embodies some slight modifications which have been found advantageous—should be of interest.

The apparatus is shown in the diagram and is drawn to scale. It consists essentially of a glass rod plunger A passing through the central tube B C, which is sealed inside the outer tube D E by a ring seal at D. The orifice of the instrument is the concentric space between A and B C and is adjusted by sliding A through the rubber bung to the required position. A thin film of glycerin on the rod facilitates its movement through the bung. The advantage of this apparatus lies in its flexibility. If a plunger fitting closely within B C is chosen it is possible to obtain a large deflection in the manometer for a flow of 0·1 ml. per min. By suitable adjustment the same plunger can give a satisfactory scale reading up to about 15 ml. per min. By choosing narrower plungers, much higher rates of flow can be measured. A Marriotte bottle affords a convenient means of calibrating the apparatus.

It is of interest to note that the Pig Iron Sub-Committee of the Iron and Steel Institute‡ has recently recommended a flowmeter for use in the determination of sulphur in pig iron by the combustion method. The White-Wright flowmeter, apart from its other advantages, is a more compact instrument than the one recommended, and has in fact been used for some time in the writer's laboratory for similar determinations.

When the apparatus is used for micro-combustions it is usual to adjust the flow by a Pregl screw clip clamped at a convenient point on the base of the flowmeter. Occasionally irregularities in the control arise, due to hysterisis effects of the rubber connection, and the liquid may be blown out of the manometer. It has been found advantageous to incorporate the splash-head trap at F, which prevents this nuisance. A trace of a wetting agent in the manometer fluid helps to prevent "sticking."

The dimensions are not critical. The tube B C is about 3 mm. diameter, and if very slow rates of flow are to be measured the plunger should be chosen to fit this closely before the apparatus is made. The overall height of the apparatus is about 32 cm., the width of the manometer 2½ cm., the bulb F 2½ cm. diameter, and the tube about 7 mm. wide. If the flowmeter is to be used for measuring different rates of flow, it will be found convenient to etch marks on the plunger corresponding to the speeds to be measured.

Microchemical Group

At the Inaugural Meeting of the Microchemical Group of the Society of Public Analysts, held on Wednesday, 4th October, the following Office-Bearers were elected: *Chairman*, H. V. A. Briscoe, A.R.C.S., D.Sc., F.R.I.C. *Vice-Chairman*, N. Strafford, M.Sc., F.R.I.C. *Hon. Secretary*, R. Belcher, F.R.I.C. *Ordinary Members of Committee*, J. G. A. Griffiths, B.A., Ph.D., F.R.I.C., Miss I. H. Hadfield, M.Sc., Mrs. J. W. Matthews, B.Sc., Ph.D., F.R.I.C., C. Whalley, B.Sc., A.R.I.C., C. L. Wilson, M.Sc., Ph.D., A.R.I.C., and G. H. Wyatt, B.Sc., Ph.D., F.R.I.C.

* *Ind. Eng. Chem., Anal. Ed.*, 1941, **13**, 574; 1943, **15**, 476.
† White and Wright. *Can. J. Res.*, 1936, **14B**, 427.

‡ "The Determination of Sulphur and Phosphorus in Pig Iron." *Iron and Steel Institute*, 1944.

METALLURGICAL DIGEST

Solubility of Hydrogen in Molten Copper-Tin Alloys

By M. B. Bever and C. F. Floe

THE solubility of hydrogen in molten copper-tin alloys is of both practical and theoretical interest. From a practical standpoint, data on the equilibrium solubility as a function of temperature, pressure and alloy composition are valuable for a better understanding of porosity problems in bronze castings, and from the theoretical point of view the determination of the hydrogen-copper-tin equilibrium is of interest since it extends the laws governing the solution of gases in metals. The results are, therefore, given of an investigation of the solubility of hydrogen in representative compositions of the copper-tin system at temperatures ranging from above the liquidus to 1300° C. and at pressures from less than 50 mm. of mercury to about atmospheric.

The apparatus used for the determination of solubility was based on a principle first developed by Sieverts. This method determines the solubility by finding the difference between the volume of soluble gas admitted to the furnace at a certain temperature and pressure and the so-called "hot volume," which is the volume of an insoluble gas—nitrogen, argon or helium—necessary to fill the furnace under the same conditions. By using capillary tubing and charging the furnace to capacity it was possible to keep the hot volume low, and in none of the tests did it exceed 20 cc. and in most of the tests it was of the order of 12 to 14 cc. A low hot volume is desirable because it increases the accuracy of the solubility determinations. The molten alloys used were prepared from high-purity electrolytic copper and from high grade tin containing less than 0·007% impurities and were thoroughly deoxidised with hydrogen before testing.

The solubility of hydrogen in pure copper between 1100° and 1300° C. is nearly directly proportional to temperature and within fairly close limits the values determined in two previous investigations are confirmed. The solubility of hydrogen in copper at 1200° C. is proportional to the square root of pressure within the limits of experimental error. The experiments on the solubility of hydrogen in pure tin indicate definite though very small solubilities. In evaluating these latter determinations the values obtained at 1100°, 1200° and 1300° C. are larger than the probable combined errors in the measurements of volumes, pressures and temperatures and these values also exceed the probable effects of diffusion and of any difference in the thermal properties of hydrogen and nitrogen. They are, however, of negligible magnitude compared with the solubilities in copper and copper-tin alloys.

The solubility of hydrogen in copper-tin alloys at 1200° C. and various pressures is given in Table I and the solubility at one atmosphere pressure and various temperatures in Table II. From the data in the latter table it is seen that the solubility as a function of alloy composition decreases with increasing tin content. In convential units and in basic units the curves representing the functions consist of two nearly linear parts, which have considerably different slopes and intersect sharply at about 25 atomic per cent. of tin, which intersection lies at or close to the composition of Cu_3SN. The solubility of hydrogen in copper-tin alloys measured at 1200° C. is proportioned to the square root of the pressure, similar to its solubility in pure copper and is in accordance with Sievert's law.

From a practical point of view, it is of interest to determine whether the addition of tin to molten copper reduces the amount of hydrogen soluble in the melt to any significant extent. In Table III is given the effect of additions of tin in reducing the solubility of hydrogen when 5·9 and 11·5% respectively are added to copper. In spite of the reductions shown the amounts of hydrogen that are soluble even with such low partial pressures of hydrogen as occur in furnace atmospheres are substantial, particularly in terms of actual volumes at high temperatures. While a complete quantitative understanding will also require data on the solubility of hydrogen in solid bronze, the investigation reported here points definitely to hydrogen as a major cause of porosity in bronze castings.

TABLE I.—SOLUBILITY OF HYDROGEN IN COPPER-TIN ALLOYS AT 1200° C. AND VARIOUS PRESSURES.

Tin Per cent.	Pressure Mm. of Hg.	H_2 per 100 cm. of Metal. C.C.
5·9	3·4	0·36
	166·3	2·95
	236·9	3·57
	524·3	5·28
	750·6	6·38
11·5	5·0	0·41
	247·7	3·04
	468·1	4·17
	763·1	5·42
21·7	62·8	1·10
	437·6	2·94
	764·0	3·91
40·2	26·5	0·35
	423·1	1·16
	771·2	1·53
54·8	26·2	0·15
	237·4	0·64
	404·0	0·81
	745·4	1·19

TABLE II.—SOLUBILITY OF HYDROGEN IN COPPER-TIN ALLOYS AT ONE ATMOSPHERE AND VARIOUS TEMPERATURES.

Wt. Per cent. Sn	Atomic Per cent. Sn	1000° C.	1100° C.	1200° C.	1300° C.
5·9	3·3	—	4·80	6·28	7·81
11·5	6·5	3·99	4·11	5·35	6·85
21·7	12·9	2·11	2·97	3·94	5·10
40·2	26·4	0·53	0·94	1·50	—
54·8	39·3	0·50	0·76	1·15	1·61

TABLE III.—EFFECT OF ADDITIONS OF TIN IN REDUCING THE SOLUBILITY OF HYDROGEN IN COPPER-RICH COPPER-TIN ALLOYS

Degs. C.	Per cent. Reduction in H_2 Solubility	
	5·9% Sn added	11·5% Sn added
1100	−16·2	−28·2
1200	−14·5	−27·2
1300	−16·7	−26·9

A.I.M.M.E. Technical Publication No. 1703, 11 pages, From *Metals Technology*, 1944, vol. 11, No. 3.

Particle Size Determination for Metal Powders

ALTHOUGH size determination of all particles is an important step in powder metallurgy, of particular value is the determination of size disbution of particles that pass through a 325 - mesh screen. There are a number of different methods available for sizing fine powders. These are microscopic; air elutriation; liquid elutriation; and gravitational fractionation.

Microscopic particle size measurements are made by counting the number of particles having a predetermined size range in any single field of observation. The size ranges are usually in steps of either 5 or 10 microns. The count by its very nature is statistical, requires a trained technician and is time consuming. It is further, difficult to interpret the results of a microscopic count. For example, the dimension measured may be considered to be the average diameter of a sphere. Based upon this assumption, the specific volumes and specific areas can be calculated. For some powders this assumption is approximately correct, but for others, electrolytic powders, for instance, such an assumption is highly inaccurate since these powders tend towards flat-plate or needle-like structures.

Sizing by air elutriation, or more commonly, air separation, depends on floating the particles in an air stream of controlled velocity. For perfectly spherical particles, this method can be made quite accurate. By varying the air velocity from some minimum to some maximum, particles of different size ranges can be separated. The weight of each fraction can then be determined. However, since it is rare that powders are even nearly spherical, errors enter due to variation in specific area for particles of a given weight. Sizing by liquid elutriation is subject to the same general objections as by air separation and is, in addition, far slower than air elutriation. Gravitational fractionation methods can be divided into two broad classes: (1) Sedimentation tests where the time for a given volume of powder to fall a fixed distance is noted. The settled powder is then removed and weighed. This type of test gives a particle size which is an average for an actual range. The size calculated is then the size of the particles if they were spherical. This is also true of the number of particles calculated on the basis of an equivalent size. This class of fractionation is relatively accurate as to duplication of results, but it is slow. (2) Methods where the metal particles, after falling some known distance, interfere with a light beam focused on a photosensitive device, causing variations in the output of the photosensitive cell. This method is susceptible to the same criticisms as the first method, but can be made to be much more rapid. If a light source and photosensitive device is placed at some fixed place along the liquid column, the change in output of the photo-tube can be used for determining the time increment for each range of particles and as short a time increment as is desired can be used. This device consists of a long glass tube, 1 cm. inside diameter, on top of which is placed a small mixing chamber, connected to the tube by a rubber connection and provided with a pinch-cock on the rubber connection and a stopper for the open end of the tube. A 6-volt, 23-candle power bulb is used as a source of light with a selenium photoelectrical cell as the light-sensitive pick-up. The distance of fall is 30 cm. for most powders, although it may be varied at will. Slits at the light source and at the photoelectric cell are provided so that there is just 1 cu. cm. of suspension for the light to pass through. The light source for the photo-cell is calibrated by measuring the out-put of the photo-cell, when a clear liquid only is interposed between the light and the cell. A resistance in the light circuit is used to vary the intensity of the light to provide correction when necessary. A small rectangular flask is interposed between the light source and the tube to provide cooling for the light beam. The suspending medium will vary for different metals, and even for the same metal, when there is a marked change in particle shape. For finely divided tungsten and molybdenum, acetone has been found to be the most satisfactory. For iron and copper powders made by oxide reduction, a mixture of 50% by volume soya bean oil and 50% by volume acetone. Electrolytic iron, on the other hand, works best in a mixture of about 25% bean oil and 75% acetone. In many cases the metal powder is not thoroughly wet by the liquid. In those instances a wetting agent must be used

From *The Iron Age*, June 15, 1944.

Why not a 50-50 Cobalt Copper Alloy?

By Colin G. Fink and J. Laurence Hutton

TO prepare a workable alloy of equal parts of copper and cobalt has so far not met with success when resorting to ordinary fusion processes. Accordingly attempts were made to prepare such an alloy by co-deposition and by powder metallurgy.

Co-deposition of Cobalt and Copper

The co-deposition of nickel and copper has been successfully carried out by a number of investigators. The co-deposition of cobalt and copper was not successful from cyanide baths, however no reports were found in literature on the use of sulphate solutions for this purpose, and it seemed of interest to determine how and how much cobalt will deposit with copper from a sulphate bath.

Experiments were carried out, but in spite of wide variations of plating conditions in the sulphate bath no true alloy (of, say, 25 to 75% copper and the balance cobalt) was obtained by deposition. It was found that the deposit was either substantially cobalt or substantially copper, depending upon relatively slight variations in pH, current density, bath temperature, and metal ion concentration and proportion. It is indicated that the cathode product is largely a matter of cathode film pH and proportion of cobalt to copper ion concentration. It would seem possible to obtain by co-deposition a true cobalt-copper alloy, of, say, equal parts by weight, provided the cathode film pH and the cobalt to copper ion proportion were closely regulated and controlled.

Application of Powder Metallurgy

The report incorporates the results of microscopic examination and some physical tests of a series of cobalt-copper alloys prepared from powders which were compacted at pressures ranging from 1 to 100 tons/sq. in. and sintered in hydrogen at temperatures from 900° to 1090° C. Further research

From a paper presented at the 85th meeting of the Electrochemical Society. (Preprint 85-18.)

was directed toward the determination of maximum mutual solubility of the two metals. For this purpose two series of alloys were prepared; one rich in copper, the other rich in cobalt, with the following compositions: 3%, 5%, 10%, and 25% cobalt and 5%, 10%, and 25% copper respectively.

It was found that solubility of copper in cobalt was nearly 10% at room temperature, while solubility of cobalt in copper was probably less than 3%. Even with this low concentration of cobalt, fine suspensions of individual particles could be distinguished in the grains of copper. Cold work prior to alloying did not apparently affect solubility.

The presence of a solid solution or of a compound was suspected in 5C–50 alloys heated to the melting point of copper or above, but the real nature of this constituent could not be established. Alloys consisting of 3% cobalt and 97% copper exhibited a high degree of plasticity in rolling. They could be reduced into strips 40 times thinner than the pellets.

The Notched Bar Impact Test

By J. H. Hollomon

AN interpretation of the brittle failure of some steels in notched-bar impact tests is presented, based upon the effects of the stress distribution present at the base of the notch, and the effects of high rates of strain and low temperatures on the properties of several typical steels. The effect of a notch in a square bar during bending may be summarised as: (1) The longitudinal tensile strength at the base of the notch is increased, and the concentration of this stress depends upon the ratio of the depth of the notch to its radius for a constant form of notch. (2) The elastic-strain rate at the base of the notch is greater than the strain rate in the unnotched section and is equal to the stress-concentration factor multiplied by the strain rate. (3) The notch introduces a sharp gradient in the shear-strain energy just below the notch. (4) Because of the presence of a transverse tensile strength the longitudinal tensile stress necessary for yielding is increased and the magnitude of this increase depends both on the stress concentration factor and the ratio of notch radius to bar width.

A correlation of tensile and impact properties is obtained from experiments carried out on a specimen of chrome - molybdenum - vanadium steel either air-cooled from above the critical temperature or water quenched from the same temperature. Both sets of specimens were tempered to about the same yield strengths. Determinations were made on the effect of prior deformation on fracture stress at − 190° C., on the effect of decreasing temperature on tensile properties at a strain rate of 10 sec.$^{-1}$ on the effect of temperature on notched-bar impact energy and on the variation of impact energy with temperature. Brittle failure was found to be due primarily to the small separation between the yield strength and the fracture strength of the undeformed metal and to the increase in the longitudinal tensile strength necessary for yielding induced by the transverse constraint imposed by the notch.

Increasing the width of a notched-bar specimen, in general, will increase the volume of material suffering deformation and thereby increase the energy required for fracture. If the ratio of notch radius to the width of the bar is below about 1–10, and the stress concentration factor is above about 2·5, the principal effect of varying the radius will be to change the rates of strain, and the primary effect of changing the width of the bar is to change the volume of material undergoing deformation. If, however, the rates of notch radius to bar width is greater than about 1–10, or the stress-concentrations factor below 2.5, increasing the radius of the notch will decrease both the strain rate and the longitudinal stress necessary for yielding, and changes in the width of the bar will produce changes in transverse constraint sufficient to affect appreciably the temperature of brittle failure, as well as to change the volume of the material suffering deformation. The strain rate at the base of the notch may, therefore, be increased by changing the geometry of the test bar or by increasing the velocity of the impact. Increasing the radius of the curvature of the notch will serve primarily to decrease the strain rate, and for conditions of geometry outside a ratio of notch radius to bar width less than 1–10 and a stress concentration factor greater than 2·5, increasing the radius of the notch will also decrease the transverse stress. Decreasing the temperature and raising the strain rate are equivalent in their effects and serve to decrease the separation between the yield strength and the fracture strength of the undeformed metal. Some steels do not break brittlely in the impact test, and these same materials maintain their ductility in simple tension to very low temperature or to very high strain rates.

The interpretation of the impact test presented and the relations between the variables of the test should aid the designer of engineering structures in choosing the conditions of the notched-bar test so that the value of the impact energy may be a relative measure of the suitability of the various steels for particular engineering applications.

From *Metals Technology*, 1944, vol. 11, No. 3 A.I.M.M.E. Technical Publication No. 1667, 25 pages

Tool Tipping by Arc Welding

By G. W. Given

THE tipping of low-carbon shanks with high-speed bits or inserts has been widely practised, particularly in the case of tools for heavy planers and lathes. The two most common methods of tipping have been brazing and cementing, the latter carried out with a proprietary cement. Both methods are well known and have given good results when properly handled, but both brazing and cementing require considerable skill and practice, and this fact has led to the development of arc welding technique for tipping.

The problem of arc welding involves the following three factors: (1) To weld without drawing the hardness of the tip, (2) Prevention of cracks in the tip or at the weld and (3) Shank design. Various types of welding rod were used experimentally to determine which produced the best results. These included 18–4–1 high carbon, 18–8 stainless, 25–12 stainless and mild steel. High-carbon welding rod was least successful and tests with 18–4–1 were limited, so that no fair conclusion could be drawn. Mild steel rod was fair and 18–8 and 25–12 stainless worked out best. A $\frac{1}{8}$ in. diameter welding rod was used in all the tests which were made between 90 and 130 amperes with reversely polarity using a standard welding machine. Results

From *Metals and Alloys*, 1943, vol. 19, No. 4, pp. 856–858.

indicated the best setting to be between 90 and 100 amperes.

In the preparation of the tip and shank contacting surfaces should be reasonably flat, but need not be precision ground. Both should have a 45° bevel or a $\frac{3}{16}$ in. radius. In welding, a single bead is laid around all four sides of the tip, or in the case of radius tools around the entire tip, and the tool is allowed to air cool after welding before grinding. In the original tests many precautions were taken in the form of preheating and slow cooling and much work was done on the basis of running two beads instead of a single bead.

Cracking of the tip was found to be discouragingly common during or immediately after running the second bead and no amount of preheating or slow cooling appeared to help, whereas trouble was rarely experienced after running the first bead. With regard to shank design some modification from conventional practice was found to be necessary and shanks were made of normalised low alloy steels.

Fluoroscopic Inspection of Light Metal Castings

By R. Taylor

INSPECTION of light metal castings for internal flows is conventionally done by radiography. At the present time, however, considerable research is being carried out to establish the best operating conditions for the fluoroscopic inspection of aluminium and aircraft castings. In anticipation that specifications will soon be issued to include fluoroscopy for routine control inspection of certain types of castings, X-ray equipment has been designed suitable either for fluoroscopic inspections alone or by means of electronic attachments for optional fluoroscopic or radiographic examination. The latter type of equipment are conveyerised for high production requiremnets.

In evaluating fluoroscopy, it is first essential that the sensitivity of the process be thoroughly and accurately determined. The standard sensitivity gauge specified by various testing authorities is called the penetrameter and is essentially a basic calibration device. If the penetrameter sensitivity is given as 2% it does not necessarily mean that the micro-shrinkage is 2%, as there are such factors as scattered radiations within a casting which must be considered. If a particular casting were made having an acceptable degree of micro-shrinkage, produced or shown on a film or screen, with a penetrameter sensitivity of 2%, it would be safe in employing the technique used for the exposure of that particular casting for 2% sensitivity.

Penetrameter sensitivity is not necessarily the sensitivity of a particular discontinuity, but rather the sensitivity that would be shown if a penetrameter wedge of the same alloy were radiographed or fluoroscoped with the same kilovoltage, milliamperage, focus-film distance and time of exposure. The sensitivity obtained is as a rule, inferior to the penetrameter sensitivity, owing to the presence of scattered radiations and unfavourable overlapping of sections of the castings. If, for example, sections 0·5 in. and 1 in. overlap, the technique is required to give a penetrameter sensitivity for 1½ in. which is capable of revealing a slot 0·03 in. deep, but this means no better than 6% in the 0·5 in. section and 3% in the 1 in. section. If there is considerable scattered radiation, the actual sensitivity obtained might be considerably worse.

The ability to discover a defect within a casting depends to a considerable extent on the shape and size of its image on the fluorescent screen, a fact that must be considered in stating the exact sensitivity of the method. Although the sensitivity obtained with the penetrameter is the basic calibrations factor, the characteristic differences in legibility of the images of various types of discontinuities must be considered in viewing the image. Sensitivity might be determined by actual sectioning of a casting for visual inspection of actual faults and then determining the penetrameter sensitivity required to reveal each type of flaw. If the permissible degree of micro-shrinkage, as estimated by the microscope, for a particular type of casting for a particular alloy was detected at a penetrameter sensitivity of 3%, it could be stated with certainty that the penetrameter sensitivity must be established at 3% for that type of casting, and, if a penetrameter sensitivity by fluoroscopy of 3% was visualised, when viewing a complicated casting, this would ensure a sensitivity of 5% for all parts of the casting.

A method of determining the sensitivity of an image on a fluorescent screen may be accomplished by building a step-table of the alloy to be inspected and graduating it in steps of three, varying in thickness, say from ½, to ¾ to 1 in., and then superposing over each thickness 5 penetrameters ranging from 2 to 10% in increments of 2%. By viewing the image on the screen the penetrameter sensitivity may then be determined.

The fluoroscopic method of inspection is not to be considered as a substitute to radiography but rather as a supplement to it. It is most useful as a method of preselecting castings with relatively gross defects for subsequent radiography. It is valuable for the inspection of cored passages in castings, and as a tool for the general control of foundry practice.

Properly applied it can cut down in a large measure the great amount of X-ray photographic work, now applied to light alloys, with economies in the cost of films, processing solutions and operator's time.

From *Metals and Alloys*, 1944, vol. 19, No. 4, 869–873.

"Periodic Pincer"

DEVELOPMENT by the U.S. Bureau of Mines of a device that ensures constant and controlled flow of wet-ore pulp through an orifice and thus facilitates the efficient operation of a classifier in the concentration of minerals was recently announced. The apparatus, known as periodic pincer," was produced in connection with an investigation of iron ore concentration being conducted by the Bureau at its Southern Experiment Station, Tuscaloosa, Alabama, in cooperation with the University of Alabama. The "periodic pincer" can be used both in commercial and laboratory work. It controls the flow of wet ore pulp by a periodic opening and closing of a collapsible rubber tubing which terminates an oversize orifice, the oversize opening preventing choke-ups. The device is operated by an electric motor and secures great precision of operation. When used in the laboratory the apparatus was employed to deliver as little as 50 lb. (23 kg.) of solids per hour; in thorough testing with a commercial concentrator it delivered as much as four tons per hour. It may also be applied to a wet ore feeder.

U.S. Department of the Interior Information Service, May 23, 1944.

Blast Furnace Moisture Control

By J. J. Alexander

A STUDY was made on a blast furnace of the Corrigan-McKinney plant to determmie the influence upon the furnace operation and pig iron analyses of maintenance of uniform blast moisture. To establish the performance on natural air, furnace and atmospheric data were obtained for test period I, when hourly wet and dry bulb temperature readings showed the moisture content of air to the furnace, while operating with natural uncontrolled moisture, to vary from 0·65 to 3·55 grains per cu. ft. (149 to 813 mgm./hl.) with variations of almost two grains per cu. ft. (458 mgm./hl.) within 24 hours.

Provision was made for injecting steam to the cold blast line near the blower discharge to correct hourly for variations in natural moisture until a total moisture of four grains per cu. ft. (916 mgm./hl.) was maintained. During the tests no changes were made in furnace practices to compensate for the additional moisture in the blast. The total moisture level was gradually increased to six grains per cu. ft. (1,374 mgm./hl.) during test period II. At the conclusion of the second test period, a comparison was made between the operating results of the controlled and natural moisture periods.

The most pronounced change was in the frequency of the casts having higher than desirable percentage of silicon in the iron. During the test period with natural moisture, 22·66% of the casts had 1·15% or more silicon in the iron, although the desired silicon range was from 0·65 to 0·95%. During period II, with moisture controlled, 4·5% of the casts had more than 1·15% Si in the iron. The percentage of silicon in the iron was evidently decreased by the control of the blast moisture, because 49·7% of the casts were within the desired range of 0·65 to 0·95% Si, compared to approximately 35% during uncontrolled moisture tests.

Steam was next injected to control total moisture at six grains per cu. ft. (1,374 mgm./hl.). During this time, the natural moisture was extremely variable, with changes from 0·6 to 5·2 grains per cu. ft. (137 to 1,191 mgm./hl.). The summary of silicon in the iron for this period shows that although 13·6% of the casts had more than 1·15% Si, 42·2% were within the desired range of 0·65 to 0·95%.

The total moisture in the blast was next controlled at eight grains per cu. ft. (1,832 mgm./hl.). (Test V.) During this test, the natural moisture was extremely changeable, ranging from 2·2 to 8·3 grains per cu. ft. (504 to 1,901 mgm./hl.) Furnace production during this period was 6% lower than during period IV. However, the iron analysis was considerably better than during any previous test. Only 3·1% of the casts had more than 1·15% Si in the iron, and 68·2% of the casts were within the desired range of 0·65 to 0·95% Si.

There were in all four natural moisture tests and five controlled moisture tests. Normally 18% of the casts have above 1·15% Si, compared to 6% with excessive silicon when moisture is controlled. It is apparent that excessive silicon casts are much more frequent during periods of low natural moisture during the winter than they are during the summer with fairly high natural moisture. During the uncontrolled moisture tests an average of only 44·1% of the casts had the desired 0·65 to 0·95% Si in the iron. With the moisture controlled an average of 58·6% had the desired silicon. There have been no indications that controlled moisture in the blast has any influence upon the sulphur content of the iron.

From *Iron and Steel Engineer*, February, 1944.

Permissible Stress Range for Small Helical Springs

By F. P. Zimmerli

THE experiments were carried out on 13 types of commercial steel wire such as commonly used for the manufacture of engine valve springs. The steels differed in composition, and covered the following classes:

Chrome vanadium.
Straight carbon.
Silico-manganese.
Stainless.
High Manganese.

The carbon steel wire was usually obtained in the heat-treated condition and some of the specimens were cold-drawn.

The wire diameter ranged from 0·148 in. to 0·162 in., the springs being hand coiled to produce 6 active coils with a pitch diameter of app. 1–1 in. Subsequent to coiling, the springs were hand ground and heat-treated or stress relieved in the case of pretempered wire. The springs were not pressed solid after coiling, as is usual in spring manufacture. Although this process would have increased the strength of material, the resulting inherent stresses would have made accurate determination of the load stresses impossible.

These load stresses were calculated from the Wahl formula, viz.:—

$$\text{Maximum stress} = \frac{16\,Pr}{\pi d^3}\left\{\frac{4c-1}{4c-4}+\frac{\cdot 615}{c}\right\}$$

where P = axial load in lb., r = mean radius of spring, d = wire diameter,

$$c = \frac{2r}{d}$$

This formula gives the sum of the torsion and shear stresses occurring on the inside of the spring with sufficient accuracy for our purpose. The fatigue tests were carried out on a special machine accommodating 8 springs in two banks of four. The springs were placed vertically on a rigid platform and could be compressed to different amounts by means of a central rod, the upper end of which was attached to a collar resting on the free end of the spring whilst the lower end was attached to an oscillating beam. By suitable adjustments of the length of the rods and the amplitude of swing, the springs are forced to change periodically from a given state of compression to a higher state and vice versa. The deflection of the spring being connected with the axial load by the well known formula

$$\delta = \frac{64\,n\,Pr^3}{d^4G}$$

(where n = number of coils and G = modulus of rigidity of material) the corresponding axial loads and hence the maximum stress (Wahl's formula) are known.

The tests were run at a series of increasing initial stresses and the corresponding maximum stress at which the next spring will stand 10^7 stress cycles determined. It was assumed that this endurance limit corresponded to practically indefinite fatigue life.

University of Michigan, *Research Bulletin, No. 26*, 1934. Digest by courtesy of R.T.P.3, Ministry of Aircraft Production.

The operating frequency being about 40/sec., this meant that the machine would have to operate about 70 hours continuously if the loading was satisfactory. As already stated, the springs were arranged in two banks of four and by having a 2-throw crankshaft oscillating two platforms, each bank could be subjected to a different stress range, thus cutting down the time required for a complete endurance curve.

Examination by a neon flash lamp showed the complete absence of any resonance conditions (spring surge) throughout the tests. All the broken springs were carefully examined and any evidence of failure other than by fatigue led to the exclusion of these particular tests.

Simultaneously with the fatigue tests, tension and torsion tests were carried out on straight portions of the wire subjected to similar heat-treatment as the coils. The ultimate torsion strength is calculated from the formula

$$\text{stress} = \frac{16M}{\pi d^3}$$

where M = Moment in in./lb. causing failure, d = diameter of wire. This stress is quite hypothetical, since Hooke's law no longer holds under these conditions.

The experiments show, however, that this theoretical stress has an apparent connection with the fatigue life of the spring and thus is useful for design purposes.

This is shown in the following table.

Steel No.	Torsional elastic Limit lb./sq.in. (× 1000)	Ultimate Torsional Strength lb./sq.in. (× 100) A	Endurance* stress lb./sq.in. (× 1000) B	Ratio B/A
1	107	152·5	86	0·564
1A	119	161·0	90	0·568
2	117	154·5	87	0·563
3	90	129	75	0·581
4	111·5	180	80	0·444
5	113	191	76	0·398
6	113·8	176	65	0·369
7	110	184	71	0·386
8	100	168	86	0·512
9		172	46	0·267
10	119	179	80	0·447
11	110	155	80	0·516
12	118	216	81	0·375
13	105	163	82	0·503

The endurance quoted is the upper maximum stress (Wahl formula) for a life of 10^7 cycles the minimum stress being + 20,000 lb. throughout. At 60,000 lb. minimum stress, the upper maximum is the order of 10,500 lb./sq. in. with the exception of stainless steel No. 9 (80,000 lb./sq. in.).

It will be noted that the highest endurance stress is obtained with the Cr–Va steels 1–3 and the silico-manganese steel 8. The lowest value (roughly ½ this maximum) is obtained with stainless steel No. 9.

KEY TO STEEL.

1, 1A, 2, 3	Chrome Vandium.
4, 5, 6, 7	Pretempered carbon steels.
10, 11, 12	Special carbon steels, No. 12 cold-drawn.
8	Silico Manganese.
9	Stainless.
13	High Manganese.

Other conclusions drawn by the author are :—

(1) The stress range in torsion fatigue (helical compression springs) is proportional to the ultimate torsional strength.

(2) No relation appears to exist between the proportional limit in torsion and the endurance stress range for 10^7 cycles.

(3) Cold-drawn steel spring wire, as now produced has a lower stress range than heat-treated wire of the same ultimate torsional strength. This is illustrated by No. 12, which has the highest ultimate torsional strength of all the samples and gives a very low B/A ratio.

Copper in Powder Metallurgy

AT present copper plays a most important role in the manufacture of fully 75% of all metal powder parts. The fabricating techniques employed in copper powder metallurgy fall into four general classifications: (1) The production of porous parts such as porous bearings. (2) The production of high strength, high-density parts such as tungsten-copper electrode tips. (3) The production of bi-layer and strip material, such as steel-backed copper-base bearings. (4) The production of highly porous parts such as filters. Parts having a porosity ranging from 5 to 30% can be produced in completely automatic equipment. The metal powder or powder mixture is lubricated by the addition of a volatile powder such as stearic acid, a metallic stearate, or salicylic acid, and charged into the hopper of an automatic tabletting press which compacts the powder mixture at pressures ranging from 20 to 40 tons per sq. in. (2,800 to 5,600 kg./cm.²). The pressed pieces are then heat-treated in a protective atmosphere usually produced from a combusted hydro-carbon gas.

In the production of parts having a high strength and high density, no foreign matter is allowed to contaminate the metal powder or powder mixture. Because of the necessity of lubricating the dies, these parts are produced on a semi-automatic basis. Compacting pressures for these parts ranged from 40 to 100 tons per sq. in. (5,600 to 14,000 kg./cm.²), and the sintering cycle is usually longer than for the production of porous parts. An alternative method of producing high-strength parts combines the pressing and sintering in one operation.

The manufacture of strip material and bi-layer bearings differs from standard powder metallurgical practice only in the equipment used for pressure application. Metal powder or a metal powder mixture is spread evenly over a cleaned metal strip which in some cases has been plated with a thin coat of tin, copper or nickel. The strip containing the powder is heat-treated by passage through a continuous furnace to bond the powder particles to each other and the backing strip. The bi-layer strip is then passed through rolls which compact the loosely sintered powder particles and the strip is again sintered.

Highly porous parts are produced from spherical copper powder. Small percentages of tin are either pre-alloyed or mixed with copper powder and in some cases, small percentages of a volatile powdered material. The mixture is filled into heat-resistant moulds and sintered in the uncompacted condition in a protective atmosphere at temperatures ranging up to 1,652° F. (900° C.). Porosities of 50 to 60% are possible. Porous bronze bearings are made from mixtures of copper and tin powders. In some cases these mixtures also contain small percentages of graphite.

Starter brushes on motors are now being made of a copper-carbon mixture. The use of copper has greatly increased the conductivity and life of these brushes. Many steel parts have been replaced by metal powder parts made of iron-copper mixtures. These parts, although they do not have the

From The *Iron Age*, April 27, 1944.

mechanical properties of the steel parts they have replaced, have resulted in a tremendous saving in cost and manufacturing time. The strength and life of diamond grinding wheels have been greatly increased by replacing the plastic backing with a copper base metal powder backing.

In the contact field copper is being added to refractory and to noble metals, combinations permitting the development of properties unattainable by other methods of fabrication. High-conductivity parts requiring extensive machining are being replaced by high-density copper parts produced from metal powders. Steel-backed copper-base bearings are being used extensively in the automotive industry. These bearings have a layer of sintered copper base powder on a steel backing.

Speeding Graphitisation of Malleable Iron

By C. H. Lorig

THE ultimate aim in annealing of white iron is to complete the process in the shortest possible time consistent with the production of good quality malleable. Two prime factors in the control of graphitising rates are the composition of the iron and the temperature of heating for the first stage of annealing.

In regard to composition, varying the silicon content affects the annealing rate profoundly. Laboratory experiments have shown that graphitisation decreases logarithmically with increasing silicon content, Fig. 1, and the effect of silicon, in commercial practice, is such that it requires six to eight times as long to complete the first stage of graphitisation with iron containing 0·9 to 1·1% silicon as required with an iron with 1·54 to 1·79% silicon. In the production of short cycle malleable, higher than normal silicon contents are employed to facilitate rapid annealing, and in most cases, castings are made free from primary graphite through control of the metal in the melting furnace. It is practical to obtain satisfactory castings of even fairly heavy sections, which malleablise in less than a day, by raising the silicon content and by setting up suitable melting practices.

For all practical purposes, the total carbon content of the iron has no effect on the rate of graphitisation during the first stages, but it is not clear whether carbon will affect the time required for second stage graphitisation although it appears that, if the number of graphite nodules or nuclear centres is increased progressively by higher carbon contents, the rate of graphitisation should also increase progressively. High manganese content will retard graphitisation moderately well during the first stage and very effectively during the second stage. The time required to graphitise a definite percentage of combined carbon at temperatures below the critical, increase rapidly as the manganese content is increased, Fig. 2.

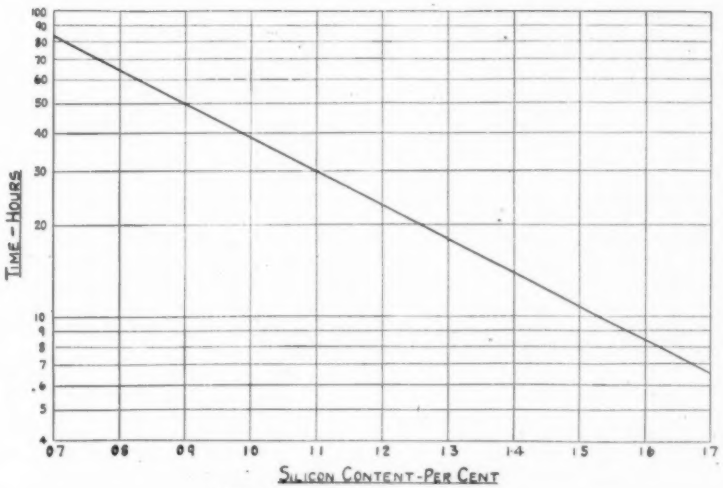


Fig. 1.—Influence of silicon.

Various alloying elements have been used in malleable iron for one purpose and another and most of them influence the graphitising time. Some are more effective in producing mottling during solidification than in producing graphitisation during the first and second stages, while others appear to be more effective in the second stage than in the first stage of graphitisation. Copper is one of the few elements besides manganese and molybdenum that may be added intentionally to malleable iron, as it not only increases mottling tendencies, but also affects the annealing behaviour by moderately reducing the stability of the carbide and therefore accelerating graphitisation in the first and second stages. 1% of copper added and the silicon content reduced by 0·1% will cause an iron to graphitise as rapidly as an additional 0·4% of silicon.

The second prime factor controlling the graphitising rate during the first stage is temperature and graphitisation proceeds at a progressively increasing rate as the annealing temperature is raised. In this respect, the temperature effect runs parallel to the silicon effect; the relative graphitising rate increasing logarithmically with temperature. Irons malleablised with a high initial annealing temperature show smaller and more numerous graphite particles than irons malleablised at a lower temperature.

Other factors that affect the graphitising rates are those associated with raw materials and the control of melting and annealing processes. Pig irons may be selected so as to obtain closely packed temper carbon nodules and steel may be added to the charge to increase the carbide retaining power. Because increasing the temperature of the molten iron has a strong carbide retaining effect, so far as mottling is concerned, it is possible with hotter iron, for the silicon content to be raised without experiencing mottling and similar effects are obtained by lengthening the time before the metal is cast. This stabilising effect on the carbides of superheat and time at superheat during the freezing of white iron is exceedingly important because of its influence on the permissible silicon

From *The Foundry*, 1944, vol. 72, No. 5, pp. 60–61, 144, 148, 150, 152, 154, 158, 160.

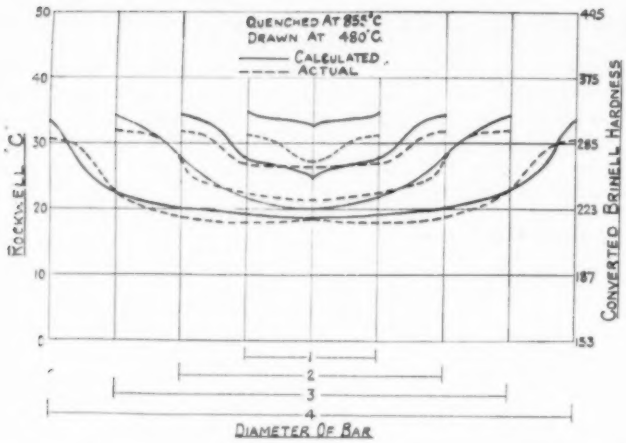


Fig. 2.—Influence of manganese (Forbes, Paulson & Minert).

content of the iron. As increased annealing rates are reflected in more more numerous and more closely packed temper carbon nodules, the effect of superheat on refining the temper carbon pattern is also important.

Copper, besides increasing the rate of annealing by virtue of its effect on the stability of the carbide, also has a definite refining action on the size of the temper carbon, and ladle additions of small amounts of aluminium, titanium, or zirconium definitely refine the white as well as the annealed structure of the iron, causing it to anneal much more readily. Various treatments such as low-temperature pouring, low-temperature preheating of the white iron, bubbling hydrogen through the iron before it is cast and quenching from above the critical temperature have all been found to have a varying effect on the graphitising rate of white cast iron.

Contact Extensometer for Measuring Working Stresses

By A. Therm and O. Svenson
Digest prepared by V. J. Ster, A.R.C.S.

ELECTRIC strain gauges with a base length of 10 to 20 mm. have reached a high state of perfection during recent years, both as regards accuracy and consistency. The complete installation is, however, complicated and the need for an electrical connection between the strain gauge proper and the rest of the rather bulky apparatus is not always easy to meet. This applies especially if the part to which the strain gauge is attached is undergoing rapid motion (rotation). Cases may obviously arise where the provision of such a cable connection becomes impossible and the method will fail, since the recording gear itself cannot be attached to the rotary part.

Now in many design problems a knowledge of the maximum and minimum working stress to which the part is subjected will suffice and the accurate variation of intermediate values with time is not required. For this purpose, the authors developed a mechanical type of strain gauge with a base length of 20 mm. Any change in this base length causes a corresponding change in an air gap between two levers forming an integral part of of the instrument frame (no pivots).

One of these levers is unaffected by any extension of the base, but its position in space is controlled by a very accurate micrometer screw. The other lever follows the motion of the movable base point with a slight magnification (2–1) an extension of the base line producing a closing of the gap. The gauge is attached to the part under investigation in the usual manner either by means of a spring clamp or welding of the base points. A zero reading of the gap is then taken by moving the adjustable lever till the gap is closed.

For this purpose the adjustable side of the gap is fitted with an insulated central electrode whilst the other side has a spring-loaded centre piece which is similarly electrically insulated.

Closing of the gap is judged by the passage of an electric current and is, recorded either by a flash lamp, telephone or other suitable devices Having thus determined the zero position corresponding to the unstrained specimen, the latter is subjected to the stress cycle requiring examination and the gap opened till a current just fails to be established. This position corresponds to the maximum strain experienced by the gauge. The minimum strain is similarly determined by closing the gap till a steady current is passed through the contacts. The micrometer screw enables these distances from the zero position to be recorded with an accuracy of $\pm 0{\cdot}4\mu$. For a base length of 20 mm., an extension of this amount corresponds to a stress of about $0{\cdot}4 kg/mm^2$ and $0{\cdot}15 kg/mm^2$ for steel and light alloys respectively, monoaxial stress being assumed. These figures therefore determine the limits of accuracy of the gauge.

It must be remembered that the electric current in this instrument only registers "on" or "off" positions and the absolute value is of no importance. The circuit is, therefore, incomparably simpler than for the standard electrical resistance gauge, where the absolute value of the current is used for measuring purposes. In the case of a rotating body, all slip rings can be avoided by using a flash lamp indicator and dry cells which are attached to the body and rotate with it. Thus during bending fatigue tests, the shaft fibres undergo periodic changes as the shaft rotates, the outer layers in the topmost position at any instance undergoing maximum extension. If the gauge together with flash lamp and battery is attached to the rotating shaft, the lamp will just light up in the topmost position if the gap setting corresponds to the maximum stress. If the gap setting is slightly smaller, the lamp traces out a circular arc, the extension of which corresponds to the period during which the shaft stress exceeds the setting. A number of such gauges should prove useful for checking up the stress distribution in any structure subject to variable load. An ordinary counter mechanism will record the number of times the stress in any part has exceeded a definite value over a period.

Z. V.D.I., vol. 88, No. 11/12, March 18, 1944, pp. 153–159. Courtesy of R.T.P.3, Ministry of Aircraft Production.